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(54) **INTERFACIAL PROCESSES FOR PREPARING PHOTOACTIVE ADDITIVES**

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(58) **Field of Classification Search**
USPC 528/196, 198; 428/220; 522/35, 111, 522/163
See application file for complete search history.

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(57) **ABSTRACT**

Different interfacial processes for producing photoactive additives are disclosed. Generally, the photoactive additives are cross-linkable polycarbonate resins formed from a dihydroxybenzophenone, a first linker moiety, a diol chain extender, and an end-capping agent. The resulting additives can be crosslinked with other polymers upon exposure to UV radiation.
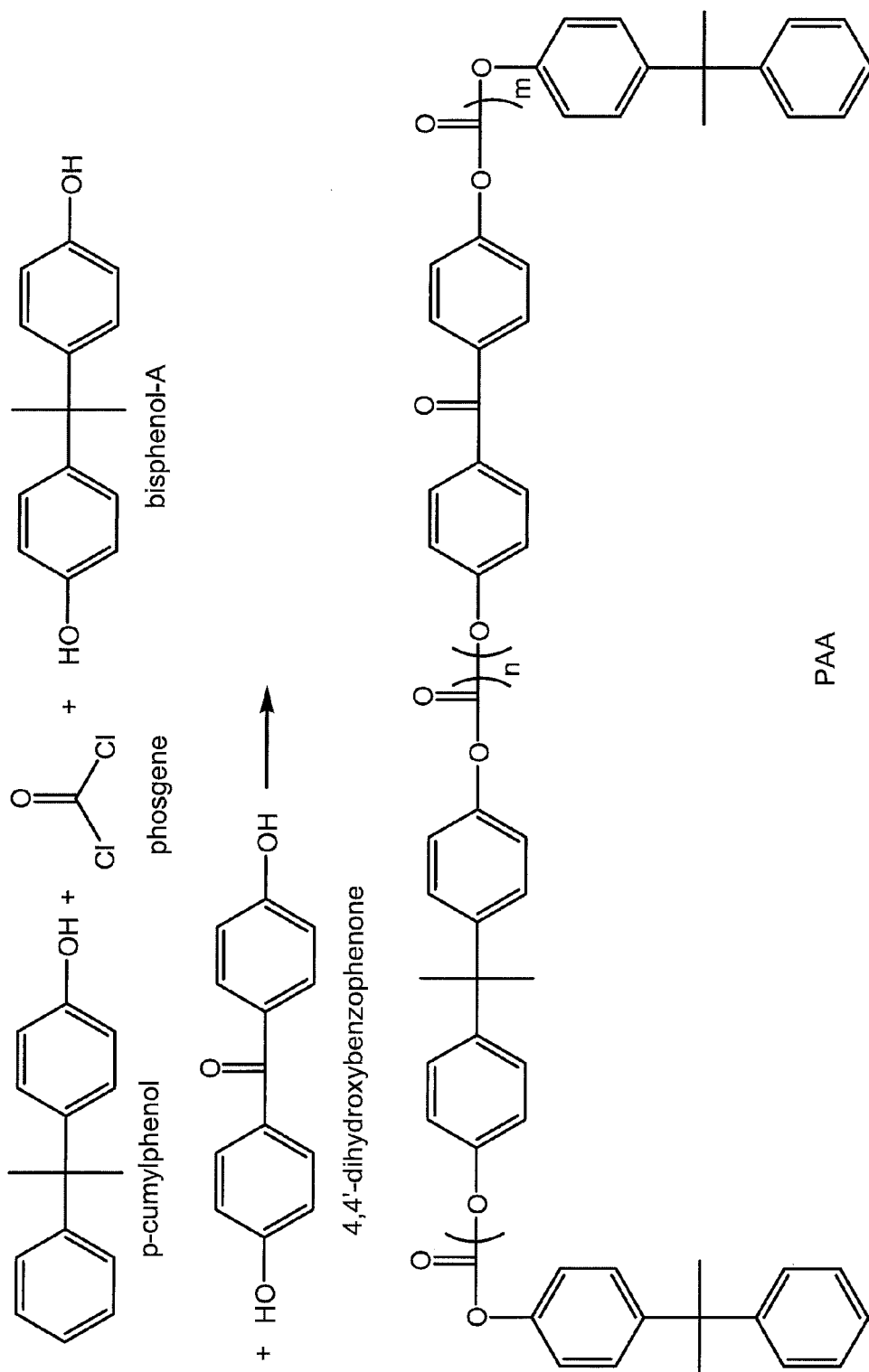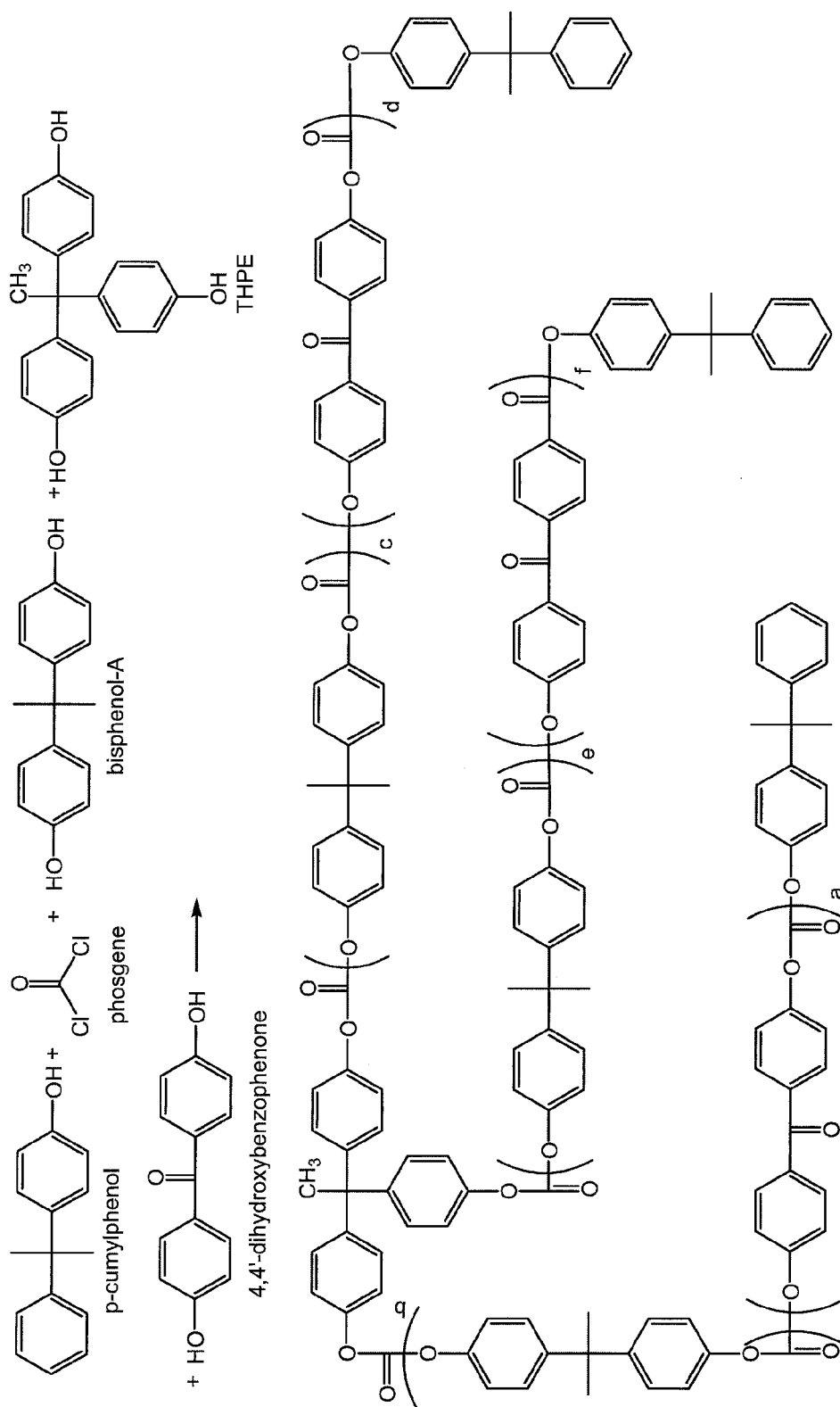
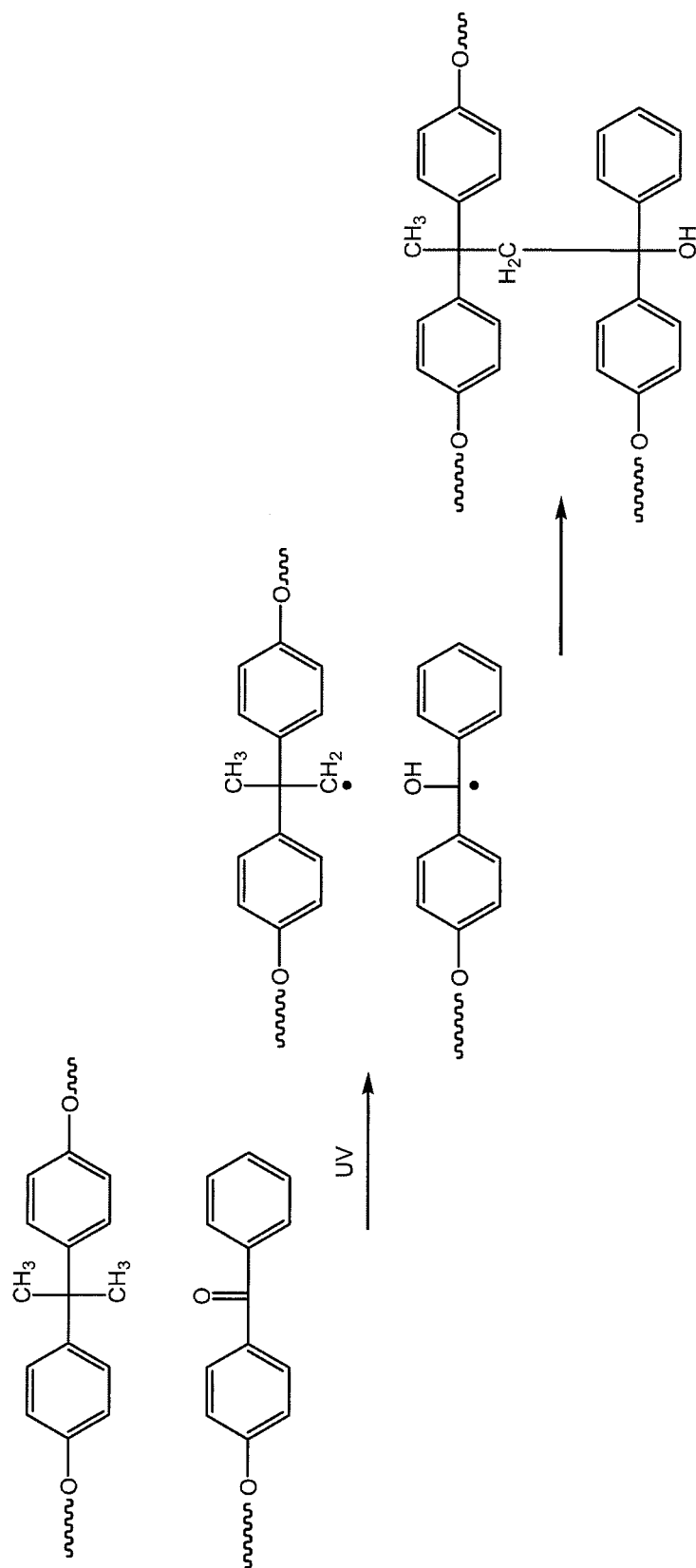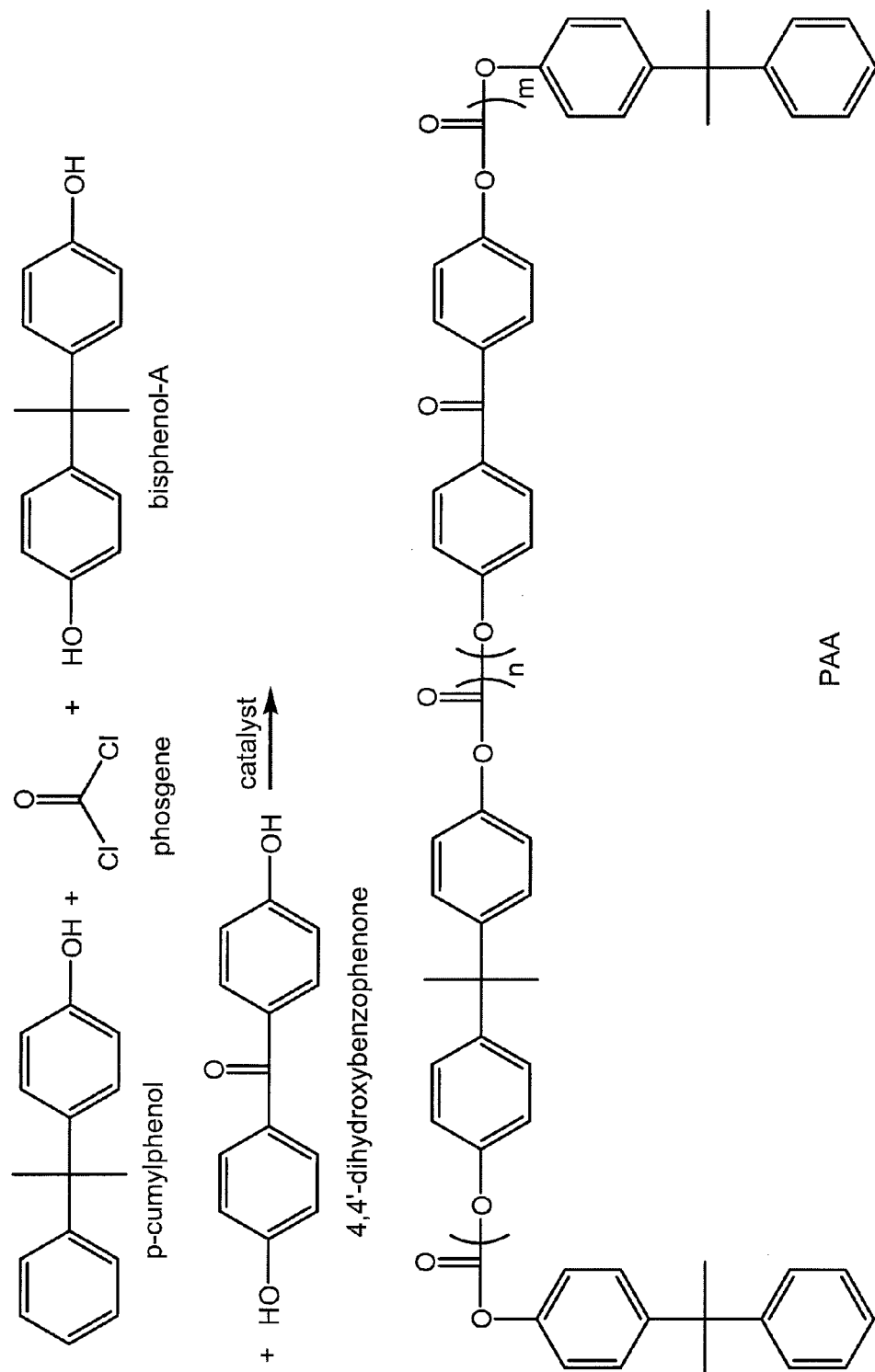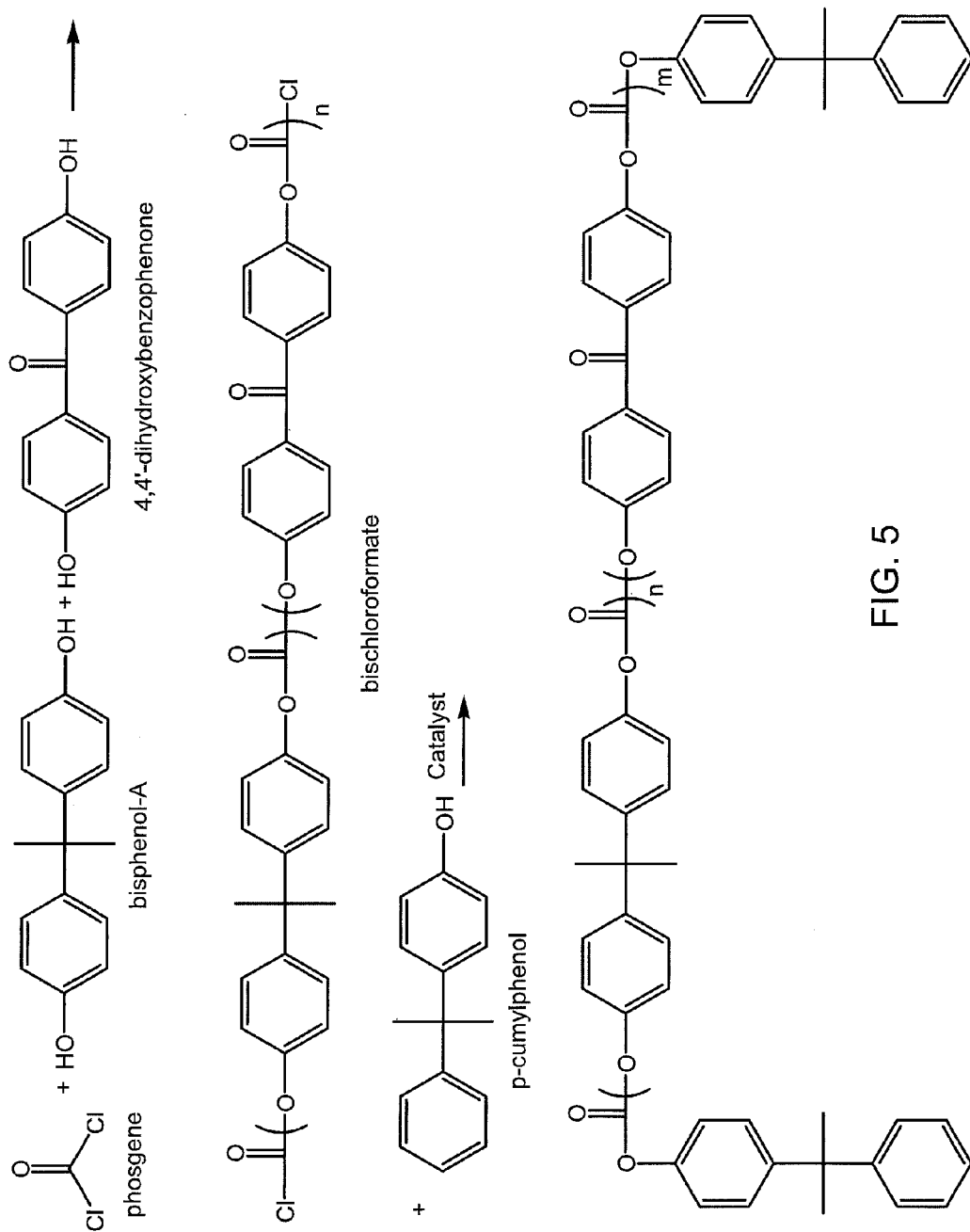**41 Claims, 6 Drawing Sheets**
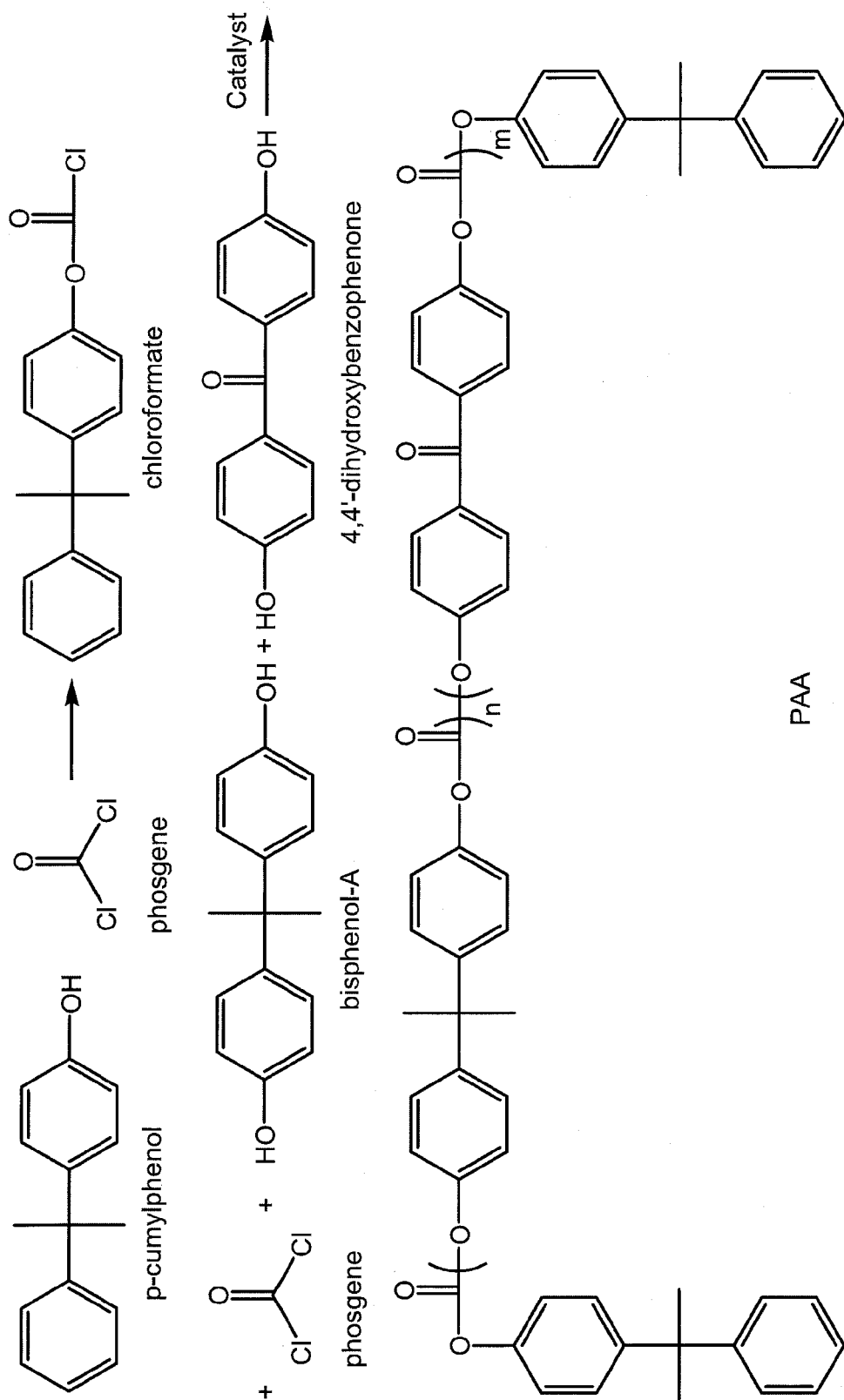
FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

INTERFACIAL PROCESSES FOR PREPARING PHOTOACTIVE ADDITIVES

BACKGROUND

This application claims priority to U.S. Provisional Patent Application Ser. No. 61/791,886, filed Mar. 15, 2013, and to U.S. Provisional Paten Application Ser. No. 61/780,222, filed Mar. 13, 2013.

The present disclosure relates to processes for producing additives that can be used to crosslink polymers, such as polycarbonate polymers, for improved properties. More specifically, the present disclosure relates to interfacial processes for making such additives.

Polycarbonates (PC) are synthetic engineering thermoplastic resins, and are a useful class of polymers having many beneficial properties. They are useful for forming a wide variety of products, such as by molding, extrusion, and thermoforming processes. Polycarbonate resins are both strong and transparent, and are used for a number of different commercial applications, including electronic engineering (E&E) parts, mechanical parts, etc. Because of their broad use, particularly in electronic applications and auto part applications, the desired properties of polycarbonates include high impact strength and toughness, heat resistance, weather and ozone resistance, and good ductility.

Polycarbonate polymers/resins and blends containing polycarbonate polymers exhibit flame retardance properties. However, such polymers drip when exposed to a flame, and this behavior worsens as the wall thickness decreases. This behavior greatly diminishes their use in transparent and opaque thin wall applications where a V0 or 5VA flame retardance rating is required. These polymers also have relatively poor chemical resistance. It would be desirable to provide additives that can improve these properties.

BRIEF DESCRIPTION

The present disclosure relates to processes for producing additives which can be used to crosslink resins (e.g. polycarbonates) and improve their flame resistance and chemical resistance. The additives are formed by the reaction of at least a first photoactive moiety with a first linker moiety. Generally, carbonate or ester linkages are found in the additives. In particular embodiments, the photoactive additives are polycarbonate polymers containing a dihydroxybenzophenone monomer that can crosslink when exposed to ultraviolet (UV) radiation.

Disclosed in embodiments herein are processes for preparing a photoactive additive from a dihydroxybenzophenone, a diol chain extender, an end-capping agent, a carbonate precursor, a base, a tertiary amine catalyst, water, and a water-immiscible organic solvent, comprising: combining the dihydroxybenzophenone, diol chain extender, tertiary amine catalyst, water, and water-immiscible solvent to form a reaction mixture; adding the carbonate precursor to the reaction mixture over a first time period while co-adding the base to regulate the reaction pH;adding the end-capping agent to the reaction mixture for a second time period within the first time period to obtain the photoactive additive while continuing to add the carbonate precursor and the base; and continuing to add the carbonate precursor and the base to the reaction mixture for a third time period after addition of the end-capping agent is complete to obtain the photoactive additive.

In particular embodiments, the carbonate precursor is phosgene, the diol chain extender is bisphenol-A, the base is an alkali metal hydroxide, and the water-immiscible organic

solvent is methylene chloride. The dihydroxybenzophenone may be 4,4'-dihydroxybenzophenone.

In some embodiments, the end-capping agent is dissolved in a solvent prior to being added to the reaction mixture, the solvent being either the water-immiscible organic solvent or water containing a base. The end-capping agent can be dissolved in a dilute aqueous sodium hydroxide solution. The solution may contain from about 1 to about 2 moles of NaOH per mole of the end-capping agent, and may contain from about 5 wt % to about 20 wt % of the end-capping agent compound.

A total time period is defined by the sum of the first time period, the second time period, and the third time period; and the second time period in which the end-capping agent is added to the reaction mixture can begin at a point from 10% to about 40% of the total time period. The reaction pH is regulated to remain between about 8.5 and about 10. The end-capping agent may be selected from the group consisting of phenol, p-t-butylphenol, p-cumylphenol, octylphenol, and p-cyanophenol.

The resulting photoactive additive may contain less than 2% of low molecular weight molecules. The resulting photoactive additive may comprise about 0.5 mole % to 50 mole % of the dihydroxybenzophenone.

The resulting photoactive additive can have a weight-average molecular weight of between 17,000 and 80,000 Daltons, as measured by GPC using a UV detector and polycarbonate molecular weight standards prior to UV exposure. Sometimes, the ratio of the PDI measured using a UV detector to the PDI measured using an RI detector is 1.4 or less when using a GPC method and polycarbonate molecular weight standards prior to UV exposure.

In particular embodiments, the resulting photoactive additive has a MFR of 1 to 40 g/10 min measured according to ASTM D1238 at 300° C./1.2 kg/360 sec dwell.

Also disclosed herein are processes for preparing a photoactive additive from a dihydroxybenzophenone, a diol chain extender, an end-capping agent, a carbonate precursor, a base, a tertiary amine catalyst, water, and a water-immiscible organic solvent, comprising: combining the dihydroxybenzophenone, diol chain extender, end-capping agent, tertiary amine catalyst, water, and water-immiscible solvent to form a reaction mixture; and adding the carbonate precursor to the reaction mixture while co-adding the base to regulate the reaction pH to obtain the photoactive additive.

In particular embodiments, the carbonate precursor is phosgene, the diol chain extender is bisphenol-A, the base is an alkali metal hydroxide, and the water-immiscible organic solvent is methylene chloride. The dihydroxybenzophenone may be 4,4'-dihydroxybenzophenone.

The end-capping agent may be selected from the group consisting of phenol, p-t-butylphenol, p-cumylphenol, octylphenol, and p-cyanophenol.

The reaction mixture may further comprise a phase transfer catalyst. In particular embodiments, the phase transfer catalyst is methyltributylammonium chloride.

The pH of the reaction mixture can be maintained from about 8.5 to about 10 while the carbonate precursor is added to the reaction mixture.

In embodiments, the carbonate precursor is added to the reaction mixture over a time period of about 15 minutes to about 45 minutes.

The resulting photoactive additive may contain less than 2% of low molecular weight molecules. The resulting photoactive additive may comprise about 0.5 mole % to 50 mole % of the dihydroxybenzophenone. The resulting photoactive additive does not contain residual pyridine.

The resulting photoactive additive can have a weight-average molecular weight of between 17,000 and 80,000 Daltons, as measured by GPC using a UV detector and polycarbonate molecular weight standards prior to UV exposure.

In particular embodiments, the resulting photoactive additive has a MFR of about 1 to about 40 g/10 min measured according to ASTM D1238 at 300° C./1.2 kg/360 sec dwell.

Also disclosed are processes for preparing a photoactive additive from a dihydroxybenzophenone, a diol chain extender, an end-capping agent, a carbonate precursor, a tertiary amine catalyst, water, and a water-immiscible organic solvent, comprising: combining the dihydroxybenzophenone, diol chain extender, water, and water-immiscible solvent to form a reaction mixture; adding the carbonate precursor to the reaction mixture to form chloroformate in the reaction mixture while co-adding the base to regulate the reaction pH; adding the end-capping agent to the reaction mixture and reacting the reaction mixture; and adding the tertiary amine catalyst to the reaction mixture and reacting the reaction mixture to obtain the photoactive additive.

In particular embodiments, the carbonate precursor is phosgene, the diol chain extender is bisphenol-A, the base is an alkali metal hydroxide, and the water-immiscible organic solvent is methylene chloride. The dihydroxybenzophenone may be 4,4'-dihydroxybenzophenone.

The end-capping agent may be selected from the group consisting of phenol, p-t-butylphenol, p-cumylphenol, octylphenol, and p-cyanophenol.

The resulting photoactive additive may contain less than 2% of low molecular weight molecules. The resulting photoactive additive may comprise about 0.5 mole % to 50 mole % of the dihydroxybenzophenone. The resulting photoactive additive can have a weight-average molecular weight of between 17,000 and 80,000 Daltons, as measured by GPC using a UV detector and polycarbonate molecular weight standards prior to UV exposure.

Also disclosed are processes for preparing a photoactive additive from a dihydroxybenzophenone, a diol chain extender, an end-capping agent, a carbonate precursor, a tertiary amine catalyst, water, and a water-immiscible organic solvent, comprising: pre-reacting the end-capping agent with the carbonate precursor in a tubular reactor to convert the end-capping agent into a monochloroformate; combining the dihydroxybenzophenone, diol chain extender, tertiary amine catalyst, water, and water-immiscible solvent in a reaction mixture; adding the carbonate precursor to the reaction mixture over a first time period; and adding the monochloroformate compound to the reaction mixture throughout the first time period while co-adding the base to regulate the reaction pH to obtain the photoactive additive.

In particular embodiments, the carbonate precursor is phosgene, the diol chain extender is bisphenol-A, the base is an alkali metal hydroxide, and the water-immiscible organic solvent is methylene chloride. The dihydroxybenzophenone may be 4,4'-dihydroxybenzophenone.

The end-capping agent may be selected from the group consisting of phenol, p-t-butylphenol, p-cumylphenol, octylphenol, and p-cyanophenol.

The resulting photoactive additive may comprise about 0.5 mole % to 50 mole % of the dihydroxybenzophenone.

The resulting photoactive additive can have a weight-average molecular weight of between 17,000 and 80,000 Daltons, as measured by GPC using a UV detector and polycarbonate molecular weight standards prior to UV exposure.

These and other non-limiting characteristics are more particularly described below.

BRIEF DESCRIPTION OF THE DRAWINGS

The following is a brief description of the drawings, which are presented for the purposes of illustrating the exemplary embodiments disclosed herein and not for the purposes of limiting the same.

FIG. 1 illustrates the formation of a photoactive additive (oligomer/polymer) from a difunctional photoactive moiety, a first linker moiety, a diol chain extender, and an endcapping agent.

FIG. 2 illustrates the formation of a branched photoactive additive (oligomer/polymer) from a difunctional photoactive moiety, a first linker moiety, a diol chain extender, an endcapping agent, and a secondary linker moiety.

FIG. 3 illustrates the crosslinking mechanism of the photoactive additive.

FIG. 4 illustrates a first process for forming the photoactive additive ("upfront" or "solution addition").

FIG. 5 illustrates another process for forming the photoactive additive through an intermediate bischloroformate.

FIG. 6 illustrates another process for forming the photoactive additive using a tubular reactor and pre-reaction of some reactants.

DETAILED DESCRIPTION

The present disclosure may be understood more readily by reference to the following detailed description of desired embodiments and the examples included therein. In the following specification and the claims which follow, reference will be made to a number of terms which shall be defined to have the following meanings.

Definitions

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. In case of conflict, the present document, including definitions, will control. Preferred methods and materials are described below, although methods and materials similar or equivalent to those described herein can be used in practice or testing of the present invention. All publications, patent applications, patents and other references mentioned herein are incorporated by reference in their entirety. The materials, methods, and examples disclosed herein are illustrative only and not intended to be limiting.

The singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise.

As used in the specification and in the claims, the term "comprising" may include the embodiments "consisting of" and "consisting essentially of." The terms "comprise(s)," "include(s)," "having," "has," "can," "contain(s)," and variants thereof, as used herein, are intended to be open-ended transitional phrases, terms, or words that require the presence of the named ingredients/steps and permit the presence of other ingredients/steps. However, such description should be construed as also describing compositions or processes as "consisting of" and "consisting essentially of" the enumerated ingredients/steps, which allows the presence of only the named ingredients/steps, along with any impurities that might result therefrom, and excludes other ingredients/steps.

Numerical values in the specification and claims of this application, particularly as they relate to polymers or polymer compositions, reflect average values for a composition that may contain individual polymers of different characteristics.

Furthermore, unless indicated to the contrary, the numerical values should be understood to include numerical values which are the same when reduced to the same number of significant figures and numerical values which differ from the stated value by less than the experimental error of conventional measurement technique of the type described in the present application to determine the value.

All ranges disclosed herein are inclusive of the recited endpoint and independently combinable (for example, the range of "from 2 grams to 10 grams" is inclusive of the endpoints, 2 grams and 10 grams, and all the intermediate values). The endpoints of the ranges and any values disclosed herein are not limited to the precise range or value; they are sufficiently imprecise to include values approximating these ranges and/or values.

As used herein, approximating language may be applied to modify any quantitative representation that may vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as "about" and "substantially," may not be limited to the precise value specified, in some cases. In at least some instances, the approximating language may correspond to the precision of an instrument for measuring the value. The modifier "about" should also be considered as disclosing the range defined by the absolute values of the two endpoints.

For example, the expression "from about 2 to about 4" also discloses the range "from 2 to 4." The term "about" may refer to plus or minus 10% of the indicated number. For example, "about 10%" may indicate a range of 9% to 11%, and "about 1" may mean from 0.9-1.1. Other meanings of "about" may be apparent from the context, such as rounding off, so, for example "about 1" may also mean from 0.5 to 1.4.

For the recitation of numeric ranges herein, each intervening number there between with the same degree of precision is explicitly contemplated. For example, for the range of 6-9, the numbers 7 and 8 are contemplated in addition to 6 and 9, and for the range 6.0-7.0, the number 6.0, 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, and 7.0 are explicitly contemplated.

Compounds are described using standard nomenclature. For example, any position not substituted by any indicated group is understood to have its valency filled by a bond as indicated, or a hydrogen atom. A dash ("-") that is not between two letters or symbols is used to indicate a point of attachment for a substituent. For example, the aldehyde group —CHO is attached through the carbon of the carbonyl group.

The term "aliphatic" refers to an linear or branched array of atoms that is not aromatic. The backbone of an aliphatic group is composed exclusively of carbon. The aliphatic group may be substituted or unsubstituted. Exemplary aliphatic groups include, but are not limited to, methyl, ethyl, isopropyl, hexyl, and cyclohexyl.

The term "aromatic" refers to a radical having a ring system containing a delocalized conjugated pi system with a number of pi-electrons that obeys Hackers Rule. The ring system may include heteroatoms such as nitrogen, sulfur, selenium, silicon and oxygen, or may be composed exclusively of carbon and hydrogen. Aromatic groups are not substituted. Exemplary aromatic groups include, but are not limited to, phenyl, pyridyl, furanyl, thienyl, naphthyl and biphenyl.

The term "ester" refers to a radical of the formula —CO—O—, wherein the carbon atom and the oxygen atom are both covalently bonded to carbon atoms.

The term "carbonate" refers to a radical of the formula —O—CO—O—, wherein the oxygen atoms are both

covalently bonded to carbon atoms. Note that a carbonate group is not an ester group, and an ester group is not a carbonate group.

The terms "carboxy" or "carboxyl" refers to a radical of the formula —COOH, wherein the carbon atom is covalently bonded to another carbon atom.

The term "alkyl" refers to a radical composed entirely of carbon atoms and hydrogen atoms which is fully saturated. The alkyl radical may be linear, branched, or cyclic.

The term "aryl" refers to an aromatic radical that is composed exclusively of carbon and hydrogen. Exemplary aryl groups include phenyl, naphthyl, and biphenyl. Note that "aryl" is a subset of aromatic.

The term "heteroaryl" refers to an aromatic radical having a ring system that is composed of carbon, hydrogen, and at least one heteroatom. Exemplary heteroaryl groups include pyridyl, furanyl, and thienyl. Note that "heteroaryl" is a subset of aromatic, and is exclusive of "aryl".

The term "halogen" refers to fluorine, chlorine, bromine, and iodine.

The term "alkoxy" refers to an alkyl radical which is attached to an oxygen atom, i.e. $—O—C_nH_{2n+1}$.

The term "aryloxy" refers to an aryl radical which is attached to an oxygen atom, e.g. $—O—C_6H_5$.

The term "hydrocarbon" refers to a radical which is composed exclusively of carbon and hydrogen. Both alkyl and aryl groups are considered hydrocarbon groups.

The term "alkenyl" refers to a radical composed entirely of carbon atoms and hydrogen atoms which contains at least one carbon-carbon double bond that is not part of an aryl or heteroaryl structure. The alkenyl radical may be linear, branched, or cyclic. An exemplary alkenyl radical is vinyl $(—CH=CH_2)$.

The term "alkenyloxy" refers to a alkenyl radical which is attached to an oxygen atom, e.g. $—O—CH=CH_2$.

The term "arylalkyl" refers to an aryl radical which is attached to an alkyl radical, with the aryl radical being appended to the parent molecular moiety through the alkyl radical, e.g. benzyl $(—CH_2—C_6H_5)$.

The term "alkylaryl" refers to an alkyl radical which is attached to an aryl radical, with the alkyl radical being appended to the parent molecular moiety through the aryl radical, e.g. tolyl $(—C_6H_4—CH_3)$.

The term "copolymer" refers to a polymer derived from two or more structural unit or monomeric species, as opposed to a homopolymer, which is derived from only one structural unit or monomer.

The term "C_3-C_6 cycloalkyl" refers to cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

The terms "Glass Transition Temperature" or "Tg" refer to the maximum temperature that a polymer, such as a polycarbonate, will have one or more useful properties. These properties include impact resistance, stiffness, strength, and shape retention. The Tg of a polycarbonate therefore may be an indicator of its useful upper temperature limit, particularly in plastics applications. The Tg may be measured using a differential scanning calorimetry method and expressed in degrees Celsius.

The glass transition temperature of a polymer, such as a polycarbonate, may depend primarily on the composition of the polymer. Polycarbonates that are formed from monomers having more rigid and less flexible chemical structures than Bisphenol-A generally have higher glass transition temperatures than Bisphenol-A polycarbonate, while polycarbonates that are formed from monomers having less rigid and more flexible chemical structures than Bisphenol-A generally have lower glass transition temperatures than Bisphenol-A poly-

carbonate. For example, a polycarbonate formed from 33 mole % of a rigid monomer, 3,3-bis(4-hydroxyphenyl)-2-phenylisoindolin-1-one ("PPPBP"), and 67 mole % Bisphenol-A has a glass transition temperature of 198° C., while a polycarbonate formed from Bisphenol-A, but also having 6 wt % of siloxane units, a flexible monomer, has a glass transition temperature of 145° C.

Mixing of two or more polycarbonates having different glass transition temperatures may result in a glass transition temperature value for the mixture that is intermediate between the glass transition temperatures of the polycarbonates that are mixed.

The glass transition temperature of a polycarbonate may also be an indicator of the molding or extrusion temperatures required to form polycarbonate parts. The higher the glass transition temperature of the polycarbonate the higher the molding or extrusion temperatures that are needed to form polycarbonate parts.

The glass transition temperatures (Tg) described herein are measures of heat resistance of, for example, polycarbonate and polycarbonate blends. The Tg can be determined by differential scanning calorimetry. The calorimetry method may use a TA Instruments Q1000 instrument, for example, with setting of 20° C./min ramp rate and 40° C. start temperature and 200° C. end temperature.

The term "halo" means that the substituent to which the prefix is attached is substituted with one or more independently selected halogen radicals. For example, "C_1-C_6 haloalkyl" means a C_1-C_6 alkyl substituent wherein one or more hydrogen atoms are replaced with independently selected halogen radicals. Non-limiting examples of C_1-C_6 haloalkyl include chloromethyl, 1-bromoethyl, fluoromethyl, difluoromethyl, trifluoromethyl, and 1,1,1-trifluoroethyl. It should be recognized that if a substituent is substituted by more than one halogen radical, those halogen radicals may be identical or different (unless otherwise stated).

The term "haze" refers to the percentage of transmitted light, which in passing through a specimen deviates from the incident beam by forward scattering. Percent (%) haze may be measured according to ASTM D 1003-07.

The term "Melt Volume Rate" (MVR) or "Melt Flow Rate" (MFR) refers to the flow rate of a polymer in a melt phase as determined using the method of ASTM D1238-10. These rates are measured by determining the amount of polymer that flows through a capillary of a specific temperature over a specified time using standard weights at a fixed temperature. MVR is expressed in cubic centimeter per 10 minutes, and MFR is expressed in grams per 10 minutes. The higher the MVR or MFR value of a polymer at a specific temperature, the greater the flow of that polymer at that specific temperature.

The term "Peak melt viscosity" refers to the highest melt viscosity value (in poise) achieved between 350° C. and 450° C. during rheological testing of a polycarbonate resin.

The term "Percent transmission" or "% transmission" refers to the ratio of transmitted light to incident light, and may be measured according to ASTM D 1003-07.

"Polycarbonate" as used herein refers to an oligomer or a polymer comprising residues of one or more monomers, joined by carbonate linkages.

"Thermal stability" as used herein refers to resistance of a polymer to molecular weight degradation under thermal conditions. Thus, a polymer with poor thermal stability may show significant molecular weight degradation under thermal conditions, such as during extrusion, molding, thermoforming, hot-pressing, and like conditions. Molecular weight degradation may also be manifest through color formation and/or

in the degradation of other properties such as weatherability, gloss, mechanical properties, and/or thermal properties. Molecular weight degradation can also cause significant variation in processing conditions such as melt viscosity changes.

The term "crosslink" and its variants refer to the formation of a stable covalent bond between two molecules. This term is intended to encompass the formation of covalent bonds that result in network formation, or the formation of covalent bonds that result in chain extension.

The present disclosure refers to "polymers," "oligomers", and "compounds". A polymer is a large molecule composed of multiple repeating units chained together, the repeating units being derived from a monomer. One characteristic of a polymer is that different molecules of a polymer will have different lengths, and a polymer is described as having a molecular weight that is based on the average value of the chains (e.g. weight average or number average molecular weight). The art also distinguishes between an "oligomer" and a "polymer", with an oligomer having only a few repeating units, while a polymer has many repeating units. For purposes of this disclosure, the term "oligomer" refers to such molecules having a weight average molecular weight of less than 15,000, and the term "polymer" refers to molecules having a weight average molecular weight of 15,000 of more, as measured by GPC using polycarbonate molecular weight standards. In contrast, for a compound, all molecules will have the same molecular weight. Compared to a polymer, a compound is a small molecule. These molecular weights are measured prior to any UV exposure.

Additives

The present disclosure relates to photoactive additives (PAA), and to compositions containing such additives. When the photoactive additive is added to one or more base resins and is then exposed to the appropriate wavelength of light, the resulting composition will have improved anti-drip and flame retardant properties compared to the base resin(s) alone or to the composition prior to the light exposure. For example, the chemical resistance, propensity to drip during burning, or the propensity to form a hole when exposed to a flame can be improved. Improved flame resistance performance characteristics may include flame out time (FOT) and time to drip (TTD). The compositions, blended or neat, can be used to provide thin-walled materials that are UL94 5VA compliant. The compositions can be used to provide thin-walled materials that are 5VA compliant and highly transparent. The compositions may also exhibit good chemical resistance, tear resistance, impact strength, ductility, hydrolytic stability, and/or weatherability. Compositions comprising a cross-linked polycarbonate formed from the PAA are also contemplated

Generally, the photoactive additives (PAA) of the present disclosure include photoactive moieties that are covalently linked together through a first linker moiety and possibly a secondary linker moiety. The photoactive moieties contain a photoactive ketone group that, when exposed to the appropriate wavelength(s) of ultraviolet light, will form a stable covalent bond between the PAA and the polymeric resin. The PAA should be stable at conventional blending, forming, and processing temperatures (i.e. stable at 350° C. or above). The PAA also should not induce the degradation of the polymeric resin with which it is blended.

The term "photoactive moiety" refers to a moiety that, when exposed to ultraviolet light of the appropriate wavelength, crosslinks with another molecule. Thus, for example, the bisphenol-A monomer in a bisphenol-A homopolycarbonate would not be considered a photoactive moiety, even

though photo-Fries rearrangement can occur upon exposure to light, because the atoms do not participate in crosslinking but merely in rearrangement of the polymer backbone.

The photoactive additive is formed from a reaction mixture containing at least a first photoactive moiety and a first linker moiety. The photoactive moiety comprises (i) a ketone group and (ii) two phenolic groups. The linker moiety comprises a plurality of functional groups that can react with the phenolic groups of the photoactive moiety. The reaction product is the photoactive additive (PAA). The molar ratio of the photoactive moiety to the linker moiety can be from 1:2 to 1:200. An end-capping agent is included in the reaction mixture. As desired, a diol chain extender can also be included. The end-capping agent and the diol chain extender do not have photoactive properties.

The term "ketone group" refers to a carbonyl group (—CO—) that is bonded to two other carbon atoms (i.e. —R—CO—R'—). The two other carbon atoms can be in an aliphatic group or in an aromatic group. An ester group and a carboxylic acid group are not considered to be a ketone group because the carbonyl group is bonded to one carbon atom and an oxygen atom.

The term "phenolic group" refers to a phenyl group (—C_6H_4—) with a hydroxyl group (—OH) covalently bonded to a carbon atom in the phenyl group.
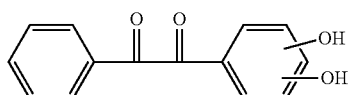
The photoactive moiety can be a dihydroxyphenone, wherein the phenolic group is directly bonded to the ketone group. Examples of such photoactive moieties include those having the structure of one of Formulas (16)-(21):
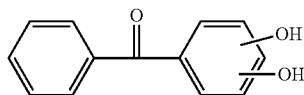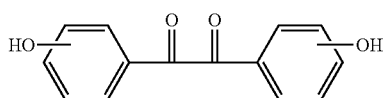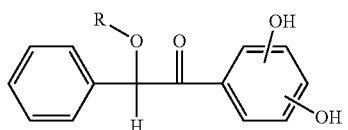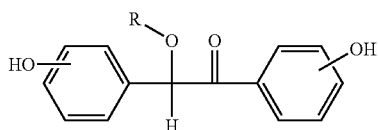
Formula (16)
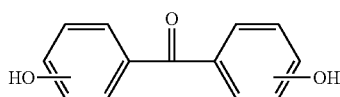
Formula (17)

Formula (18)

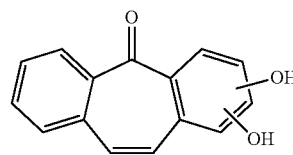Formula (19)

Formula (20)

Formula (21)

wherein R is H, alkyl, or aryl.

The compound of Formula (16) is a dihydroxyphenyl-phenylmethanone. The compound of Formula (17) is a bis (hydroxyphenyl)methanone. The compounds of Formulas (16) or (17) could also be referred to as dihydroxybenzophe-

nones. The compound of Formula (18) is a 1-dihydroxyphe-nyl-2-phenylethane-1,2-dione. The compound of Formula (19) is a 1,2-bis(hydroxyphenyl)ethane-1,2-dione. The compounds of Formulas (18) or (19) could also be referred to as dihydroxybenzils. The compound of Formula (20) is a 1-(di-hydroxyphenyl)-2-hydrocarboxy-2-phenylethanone. The compound of Formula (21) is a 1,2-bis(hydroxyphenyl)-2-hydrocarboxy-ethanone.
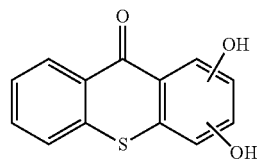
In some other embodiments, the R and R' groups attached to the ketone group form a ring structure. In such embodiments, the aromatic rings can include both aryl rings or het-eroaryl rings. Examples of such photoactive moieties include those having the structure of one of Formulas (26)-(29):
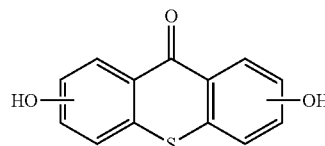
Formula (26)
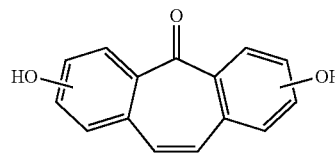
Formula (27)

Formula (28)

Formula (29)

The compounds of Formula (26) and (27) are a dihydroxy-dibenzo[1,3-e:1,2'-f][7]annulen-11-one. The compounds of Formula (28) and (29) are a dihydroxythioxanthen-9-one. The different formulas reflect the location of the two hydroxyl groups (either on the same ring, or on a different ring.

The photoactive moiety is reacted with one or more linker moieties. At least one of the linker moieties comprises a plurality of functional groups that can react with a phenolic group of the photoactive moiety. Examples of such functional groups include a carboxylic acid (and anhydrides thereof), an acyl halide, an alkyl ester, and an aryl ester. These functional groups are illustrated below in general formula (A):
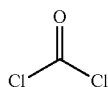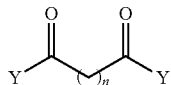
Formula (A)

where Y is hydroxyl, halogen, alkoxy, or aryloxy. The functional groups can be joined to an aliphatic group or an aromatic group which serves as a "backbone" for the linker moiety. In particular embodiments, the linker moiety can have two, three, four, or even more functional groups.
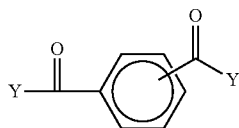
Some examples of linker moieties which have two functional groups and can react with the photoactive moieties include those having the structure of one of Formulas (30, (32), or (33):
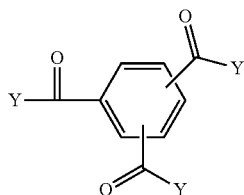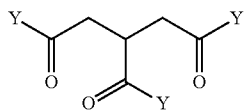
Formula (30)

Formula (32)

Formula (33)

where Y is hydroxyl, halogen, alkoxy, or aryloxy; and where n is 1 to 20. It should be noted that Formula (33) encompasses isophthalic acid and terephthalic acid.
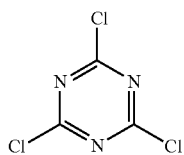
Some examples of linker moieties which have three functional groups and can react with the photoactive moieties include those having the structure of one of Formulas (36)-(38):

Formula (36)

Formula (37)

Formula (38)

where Y is hydroxyl, halogen, alkoxy, or aryloxy.

Some examples of linker moieties which have four functional groups and can react with the photoactive moieties include those having the structure of one of Formulas (39)-(41):
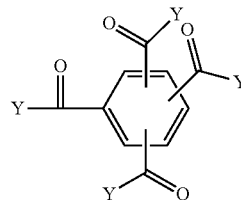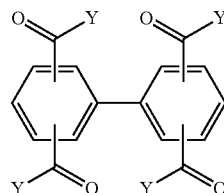
Formula (39)

Formula (40)

Formula (41)
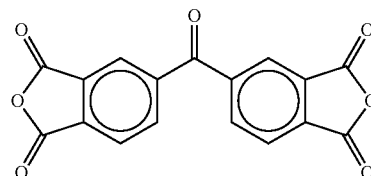
where Y is hydroxyl, halogen, alkoxy, or aryloxy.

In some embodiments, functional groups can be provided by short oligomers, including oligomers containing glycidyl methacrylate monomers with styrene or methacrylate monomers, or epoxidized novolac resins. These oligomers can permit the desired the number of functional groups to be provided. Such oligomers are generalized by the structure of Formula (42):
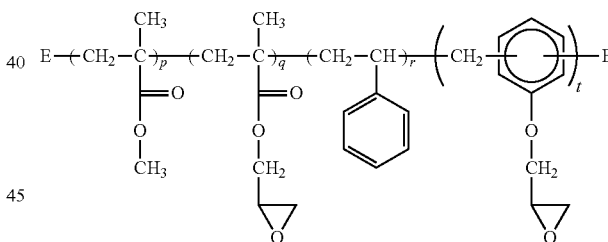
Formula (42)

where E is hydrogen or an endcapping agent, p is the number of methacrylate monomers, q is the number of methacrylate monomers, r is the number of styrene monomers, and t is the number of epoxidized novolac (phenol-formaldehyde) monomers. Generally, $p+q+r+t \leq 20$. When the oligomer contains glycidyl methacrylate monomers with styrene or methacrylate monomers, generally $t=0$ and $q \geq 1$. Similarly, for novolac resins, $p=q=r=0$. The epoxy groups can be reacted with the phenolic group of the photoactive moiety.

As discussed above, the photoactive moiety has two phenolic groups and the linker moiety has two or more functional groups. In embodiments that use only the photoactive moiety and the linker moiety in the reaction mixture, the resulting photoactive additive (PAA) will be a compound, each molecule having the same molecular weight. Again, the molar ratio of the photoactive moiety to the linker moiety can be from 1:2 to 1:200.

In particularly desired embodiments, the photoactive additive can be formed from a reaction mixture containing the

photoactive moiety, the first linker moiety, and one or more chain extenders. The chain extender is a molecule that contains only two hydroxyl groups and is not photoactive when exposed to light. The chain extender can be used to provide a desired level of miscibility when the additive is mixed with other polymeric resins. The photoactive additive may comprise from about 75 wt % to about 99.5 wt %, or from 95 wt % to about 99 mole %, or from about 80 wt % to about 95 wt %, or from about 80 wt % to about 90 wt %, of the diol chain extender.

A first exemplary chain extender is a bisphenol of Formula (B):

$$(B)$$

wherein R^a and R^b each represent a halogen atom or a monovalent hydrocarbon group and may be the same or different; p and q are each independently integers of 0 to 4; and A represents one of the groups of formula (B-1):

$$(B-1)$$

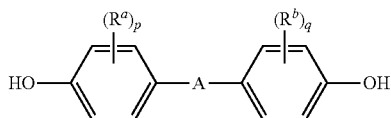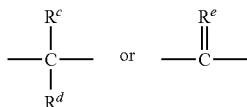wherein R^c and R^d each independently represent a hydrogen atom or a monovalent linear or cyclic hydrocarbon group and R^e is a divalent hydrocarbon group. For example, A can be a substituted or unsubstituted C_3-C_{18} cycloalkylidene.

Specific examples of the types of bisphenol compounds that may be represented by Formula (B) include 1,1-bis(4-hydroxyphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane (hereinafter "bisphenol-A" or "BPA"), 2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(4-hydroxyphenyl)octane, 1,1-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)n-butane, 2,2-bis(4-hydroxy-1-methylphenyl)propane, and 1,1-bis(4-hydroxy-t-butylphenyl)propane.
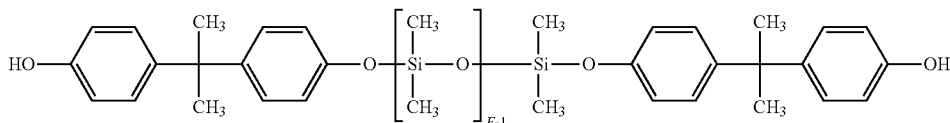
A second exemplary chain extender is a bisphenol of Formula (C):

$$(C)$$
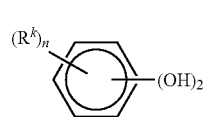
wherein each R^k is independently a C_{1-10} hydrocarbon group, and n is 0 to 4. The halogen is usually bromine. Examples of compounds that may be represented by Formula (C) include resorcinol, substituted resorcinol compounds such as 5-methyl resorcinol, 5-phenyl resorcinol, or 5-cumyl resorcinol; catechol; hydroquinone; and substituted hydroquinones such as 2-methyl hydroquinone, 2-t-butyl hydroquinone, 2-phenyl hydroquinone, 2-cumyl hydroquinone, or 2,3,5,6-tetramethyl hydroquinone.

A third exemplary chain extender is a bisphenolpolydiorganosiloxane of Formula (D-1) or (D-2):

$$(D-1)$$

$$(D-2)$$
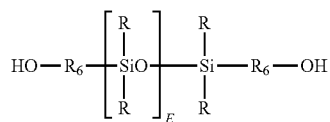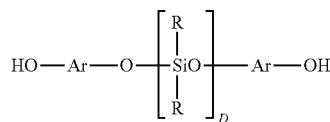
wherein each Ar is independently aryl; each R is independently alkyl, alkoxy, alkenyl, alkenyloxy, aryl, aryloxy, arylalkyl, or alkylaryl; each R_6 is independently a divalent C_1-C_{30} organic group such as a C_1-C_{30} alkyl, C_1-C_{30} aryl, or C_1-C_{30} alkylaryl; and D and E are an average value of 2 to about 1000, specifically about 2 to about 500, or about 10 to about 200, or more specifically about 10 to about 75.

Specific examples of Formulas (D-1) or (D-2) are illustrated below as Formulas (D-a) through (D-d):
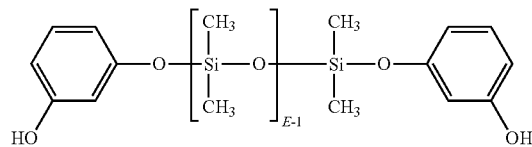
$$(D-a)$$

$$(D-b)$$

15 | 16

-continued

(D-c)

(D-d)
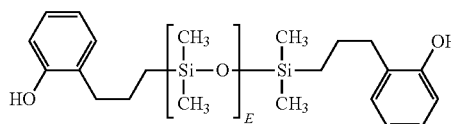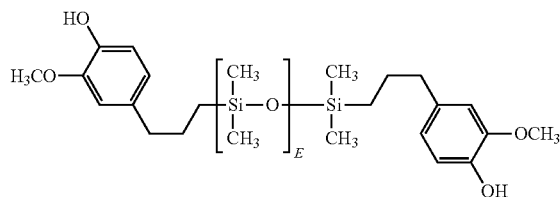
where E is an average value from 10 to 200.

A fourth exemplary chain extender is an aliphatic diol of Formula (E):

$$HO—\underset{X}{\overset{X}{C}}{}_{j}—OH \quad (E)$$
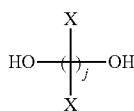
wherein each X is independently hydrogen, halogen, or alkyl; and j is an integer from 1 to 20. Examples of an aliphatic diol include ethylene glycol, propanediol, 2,2-dimethyl-pro-panediol, 1,6-hexanediol, and 1,12-dodecanediol.

A fifth exemplary chain extender is a dihydroxy compound of Formula (F), which may be useful for high heat applications:

(F)
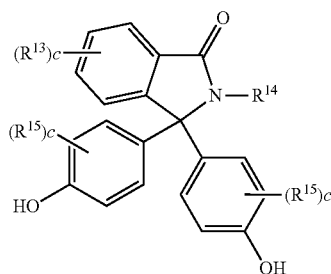
wherein R^{13} and R^{15} are each independently a halogen or a C_1-C_6 alkyl group, R^{14} is a C_1-C_6 alkyl, phenyl, or phenyl substituted with up to five halogens or C_1-C_6 alkyl groups, and c is 0 to 4. In a specific embodiment, R^{14} is a C_1-C_6 alkyl or phenyl group. In still another embodiment, R^{14} is a methyl or phenyl group. In another specific embodiment, each c is 0. Compounds of Formula (F) include 3,3-bis(4-hydroxyphe-nyl)-2-phenylisoindolin-1-one (PPPBP); 4,4'-(1-phenyle-thane-1,1-diyl)diphenol or 1,1-bis(4-hydroxyphenyl)-1-phe-nyl-ethane (bisphenol-AP); and 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane) (bisphenol TMC).

Other dihydroxy compounds (i.e. diol chain extenders) that might impart high Tgs to the polycarbonate as a copolycar-bonate are dihydroxy compounds having adamantane units, as described in U.S. Pat. No. 7,112,644 and U.S. Pat. No. 3,516,968, which are fully incorporated herein by reference. A compound having adamantane units may have repetitive units of the following formula (G) for high heat applications:

(G)
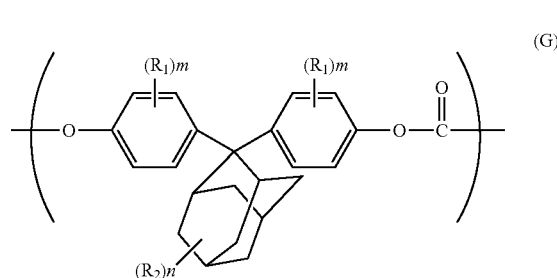
wherein R_1 represents a halogen atom, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, an aryl group having 6 to 12 carbon atoms, an aryl-substituted alkenyl group having 7 to 13 carbon atoms, or a fluoroalkyl group having 1 to 6 carbon atoms; R_2 represents a halogen atom, an alkyl group having 1 to 12 carbon atoms, an alkoxy group having 1 to 12 carbon atoms, an aryl group having 6 to 12 carbon atoms, an aryl-substituted alkenyl group having 7 to 13 carbon atoms, or a fluoroalkyl group having 1 to 12 carbon atoms; m represents an integer of 0 to 4; and n represents an integer of 0 to 14.

Other dihydroxy compounds that might impart high Tgs to the polycarbonate as a copolycarbonate are dihydroxy com-pounds having fluorene-units, as described in U.S. Pat. No. 7,244,804. One such fluorene-unit containing dihydroxy compound is represented by the following formula (H) for high heat applications:

(H)
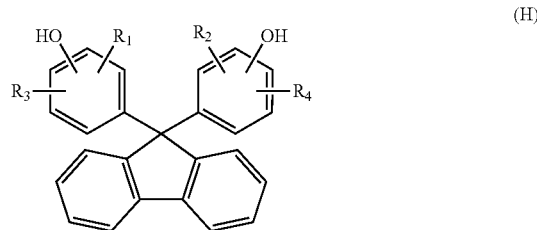
wherein R_1 to R_4 are each independently a hydrogen atom, a hydrocarbon group with 1 to 9 carbon atoms which may contain an aromatic group, or a halogen atom.

Another chain extender that could be used is an isosorbide. A monomer unit derived from isosorbide may be an isorbide-bisphenol unit of Formula (I):

(I)
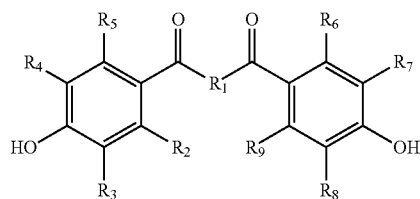
wherein R_1 is an isosorbide unit and R_2-R_9 are each independently a hydrogen, a halogen, a C_1-C_6 alkyl, a methoxy, an ethoxy, or an alkyl ester.

The R_1 isosorbide unit may be represented by Formula (I-a):

(I-a)
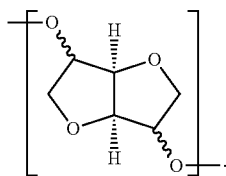
The isosorbide unit may be derived from an isosorbide, a mixture of isosorbide, a mixture of isomers of isosorbide, and/or from individual isomers of isosorbide. The stereochemistry for the isosorbide-based carbonate units of Formula (I) is not particularly limited. These diols may be prepared by the dehydration of the corresponding hexitols. Hexitols are produced commercially from the corresponding sugars (aldohexose). Aliphatic diols include 1,4:3,6-dianhydro-D glucitol; 1,4:3,6-dianhydro-D mannitol; and 1,4:3,6-dianhydro-L iditol; and any combination thereof. Isosorbides are available commercially from various chemical suppliers including Cargill, Roquette, and Shanxi. The isosorbide-bisphenol may have a pKa of between 8 and 11.

As previously explained, a first photoactive moiety is reacted with a first linker moiety to obtain the photoactive additive. In some embodiments, a secondary linker moiety is included in the reaction mixture. The secondary linker moiety has at least three functional groups, each of which can react with the functional groups of the first linker moiety, and acts as a branching agent. Generally, the functional groups of the secondary linker moiety are hydroxyl groups.

Some examples of secondary linker moieties which have three functional groups and can react with the first linker moiety include those having the structure of one of Formulas (43)-(46):
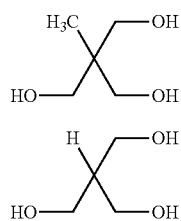
Formula (43)

Formula (44)
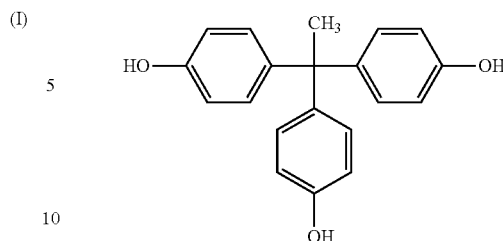
Formula (45)

Formula (46)
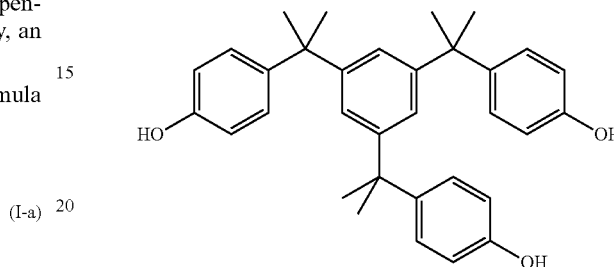
Some examples of secondary linker moieties which have four functional groups and can react with the first linker moiety include those having the structure of one of Formulas (47)-(48):
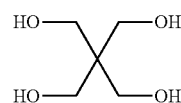
Formula (47)
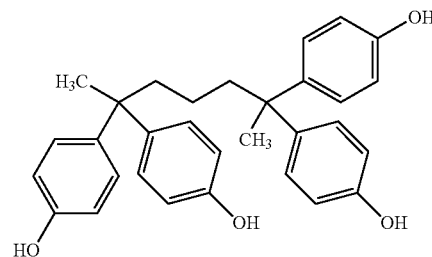
Formula (48)

In some embodiments, the secondary linker moiety can be an oligomer, made from an epoxidized novolac monomer. These oligomers can permit the desired number of functional groups to be provided. Such oligomers are generalized by the structure of Formula (49):
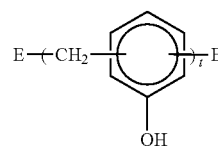
Formula (49)

wherein E is hydrogen or an endcapping agent; and t is an integer from 1 to 20.

An end-capping agent is generally used to terminate any polymer chains of the photoactive additive. The end-capping agent (i.e. chain stopper) is a monohydroxy compound, a mono-acid compound, or a mono-ester compound. Exem-

plary endcapping agents include phenol, p-cumylphenol (PCP), resorcinol monobenzoate, p-tert-butylphenol, octylphenol, p-cyanophenol, and p-methoxyphenol. If not modified with other adjectives, the term "end-capping agent" is used herein to denote a compound that is not photoactive when exposed to light. For example, the end-capping agent does not contain a ketone group. The photoactive additive may comprise about 0.5 mole % to about 5.0 mole % endcap groups derived from the end-capping agent.

Depending on the selection of the first linker moiety, the cross-linkable polycarbonate of the present disclosure may be a polyester-polycarbonate copolymer. The molar ratio of ester units to carbonate units in the polyester-polycarbonate may vary broadly, for example 1:99 to 99:1, specifically 10:90 to 90:10, more specifically 25:75 to 75:25, optionally expanded depending on the desired properties of the final composition. The polyester units may be derived from an aliphatic or aromatic dicarboxylic acid. Aliphatic dicarboxylic acids may have from 6 to about 36 carbon atoms, optionally from 6 to 20 carbon atoms. Exemplary aliphatic dicarboxylic acids include adipic acid, sebacic acid, 3,3-dimethyl adipic acid, 3,3,6-trimethyl sebacic acid, 3,3,5,5-tetramethyl sebacic acid, azelaic acid, dodecanedioic acid, dimer acids, cyclohexane dicarboxylic acids, dimethyl cyclohexane dicarboxylic acid, norbornane dicarboxylic acids, adamantane dicarboxylic acids, cyclohexene dicarboxylic acids, or O_{14}, C_{18} and O_{20} diacids. Exemplary aromatic dicarboxylic acids include isophthalic or terephthalic acid, 1,2-di(p-carboxyphenyl)ethane, 4,4'-dicarboxydiphenyl ether, 4,4'-bisbenzoic acid; 1,4-, 1,5-, or 2,6-naphthalenedicarboxylic acids; and combinations comprising at least one of the foregoing acids. A specific dicarboxylic acid mixture comprises a combination of isophthalic acid and terephthalic acid wherein the weight ratio of isophthalic acid to terephthalic acid is about 91:9 to about 2:98.

The polyester unit of a polyester-polycarbonate may be derived from the reaction of a combination of isophthalic and terephthalic diacids (or derivatives thereof) with resorcinol. In another embodiment, the polyester unit of a polyester-polycarbonate may be derived from the reaction of a combination of isophthalic acid and terephthalic acid with bisphenol-A. In an embodiment, the polycarbonate units may be derived from bisphenol-A. In another specific embodiment, the polycarbonate units may be derived from resorcinol and bisphenol-A in a molar ratio of resorcinol carbonate units to bisphenol-A carbonate units of 1:99 to 99:1.

The photoactive additives of the present disclosure can be a compound, an oligomer, or a polymer. The oligomer has a weight average molecular weight (Mw) of less than 15,000, including 10,000 or less. The polymeric photoactive additives of the present disclosure have a Mw of 15,000 or higher. In particular embodiments, the Mw is between 17,000 and 80,000 Daltons, or between 17,000 and 35,000 Daltons. These molecular weights are measured prior to any UV exposure. The Mw may be varied as desired. Polymers/oligomers with relatively higher Mw's generally retain their mechanical properties better, while polymers/oligomers with relatively lower Mw's generally have better flow properties. In some particular embodiments, the Mw of the photoactive additives is about 5,000 or less. During melt processing, oligomers are more likely to rise to the surface of the product. Long chain aliphatic diols (C_6 or higher) can also be used for this purpose. This may increase the concentration of the additive at the surface, and thus increase the crosslinking density at the surface upon exposure to UV light as well.

The product resulting from the reaction in FIG. 1 is illustrative of such photoactive additives. Here, the photoactive additive is formed from a first photoactive moiety, a first linker moiety, a diol chain extender, and an end-capping agent. 4,4'-dihydroxybenzophenone is reacted with phosgene, bisphenol-A, and p-cumylphenol (endcap) to obtain the photoactive additive.

An example of a photoactive additive formed from a first photoactive moiety, a first linker moiety, a diol chain extender, end-capping agent, and a secondary linker moiety is seen in FIG. 2. Here, 4,4'-dihydroxybenzophenone is reacted with phosgene (first linker moiety), bisphenol-A (diol chain extender), tris(hydroxyphenyl)ethane (THPE, secondary linker moiety), and p-cumylphenol (end-capping agent) to obtain the photoactive additive. Note that the THPE (secondary linker moiety) reacts with the phosgene (first linker moiety), not with the 4,4'-dihydroxybenzophenone (photoactive moiety). The resulting photoactive additive (PAA) may be an oligomer or a polymer with a weight average molecular weight and a polydispersity index.

One crosslinking mechanism of the additives is believed to be due to hydrogen abstraction by the ketone group from an alkyl group that acts as a hydrogen donor and subsequent coupling of the resulting radicals. This mechanism is illustrated in FIG. 3 with reference to a benzophenone (the photoactive moiety) and a bisphenol-A (BPA) monomer. Upon exposure to UV, the oxygen atom of the benzophenone abstracts a hydrogen atom from a methyl group on the BPA monomer and becomes a hydroxyl group. The methylene group then forms a covalent bond with the carbon of the ketone group. Put another way, the ketone group of the benzophenone could be considered to be a photoactive group. It should be noted that the presence of hydrogen is critical for this reaction to occur. Other mechanisms may occur after the initial abstraction event with base resins containing unsaturated bonds or reactive side groups.

In particular embodiments, the photoactive additives (PAAs) disclosed herein are cross-linkable polycarbonates comprising repeating units derived from a dihydroxybenzophenone monomer (i.e. of Formula (17)). These polycarbonates, prior to cross-linking, can be provided as thermally stable high melt-flow polymers, and can thus be used to fabricate a variety of thin-walled articles (e.g., 3 mm or less). These articles may subsequently be treated (e.g., with UV-radiation) to affect cross-linking, thereby providing thin-walled materials that meet desired performance requirements (e.g., 5VA performance, chemical resistance, transparency). The cross-linked materials, in addition to flame resistance and chemical resistance, may retain or exhibit superior mechanical properties (e.g., impact resistance, ductility) as compared to the composition prior to cross-linking.

The dihydroxybenzophenone monomers of the cross-linkable polycarbonates provide a reactive functional group for cross-linking the polycarbonates. For example, treatment of a cross-linkable polycarbonate of the invention with a suitable dose of ultraviolet radiation, as further described herein, may initiate cross-linking reaction between the dihydroxybenzophenone carbonyl carbon and a carbon atom of another functional group (e.g., a methylene carbon atom, such as in bisphenol-A) in the same polymer or another polymer in the composition.

The cross-linkable polycarbonates of the present disclosure include homopolycarbonates, copolymers comprising different moieties in the carbonate (referred as "copolycarbonates"), copolymers comprising carbonate units and other types of polymer units such as polyester units, polysiloxane units, and combinations comprising at least one homopoly-

carbonate and copolycarbonate. For reference, the term "dipolymer" refers to copolymers derived specifically from two different monomers, and the term "terpolymer" refers to copolymers derived specifically from three different monomers

If the cross-linkable polycarbonate is a copolymer, the monomers may be randomly incorporated into the polycarbonate. A random copolymer may have several block sequences and alternate sequences that follow a statistical distribution. In a random x:(1−x) copolymer, wherein x is the mole percent of a first monomer and 1−x is the mole percent of the other monomers, one can calculate the distribution of each monomer using peak area values determined by ^{13}C NMR, for example. The copolymer can be an alternating copolymer with alternating I and O units (—I—O—I—O—I—O—I—O—), or I and 0 units arranged in a repeating sequence (e.g. a periodic copolymer having the formula: (I—O—I—O—O—I—I—I—I—O—O)n). The cross-linkable polycarbonate copolymer may be a statistical copolymer in which the sequence of monomer residues follows a statistical rule. The copolymer may also be a block copolymer that comprises two or more homopolymer subunits linked by covalent bonds (—I—I—I—I—I—O—O—O—O—O—). The union of the homopolymer subunits may require an intermediate non-repeating subunit, known as a junction block. Block copolymers with two or three distinct blocks are called diblock copolymers and triblock copolymers, respectively.

In embodiments, the cross-linkable polycarbonates of the present disclosure contain from about 0.5 mole % to about 50 mole % of the dihydroxybenzophenone monomer (i.e. repeating units derived from the dihydroxybenzophenone monomer). In more specific embodiments, the polymers contain from about 1 mole % to about 3 mole %, or from about 1 mole % to about 6 mole %, from about 10 mole % to about 25 mole %, or from about 0.5 mole % to about 25 mole % of the dihydroxybenzophenone monomer.

The cross-linkable polycarbonates of the present disclosure may have a glass transition temperature (Tg) of greater than 120° C., 125° C., 130° C., 135° C., 140° C., 145° C., 150° C., 155° C., 160° C., 165° C., 170° C., 175° C., 180° C., 185° C., 190° C., 200° C., 210° C., 220° C., 230° C., 240° C., 250° C., 260° C., 270° C., 280° C., 290° C., or 300° C., as measured using a differential scanning calorimetry method. In certain embodiments, the polycarbonates have glass transition temperatures ranging from about 120° C. to about 230° C., about 140° C. to about 160° C., about 145° C. to about 155° C., about 148° C. to about 152° C., or about 149° C. to about 151° C.

The cross-linkable polycarbonates of the present disclosure may have a weight average molecular weight (Mw) of 15,000 to about 80,000 Daltons [±1,000 Daltons], or of 15,000 to about 35,000 Daltons [±1,000 Daltons], or of about 20,000 to about 30,000 Daltons [±1,000 Daltons]. In certain embodiments, the cross-linkable polycarbonates have weight average molecular weights of about 16,000 Daltons [±1,000 Daltons], about 17,000 Daltons [±1,000 Daltons], about 18,000 Daltons [±1,000 Daltons], about 19,000 Daltons [±1,000 Daltons], about 20,000 Daltons [±1,000 Daltons], about 21,000 Daltons [±1,000 Daltons], about 22,000 Daltons [±1,000 Daltons], about 23,000 Daltons [±1,000 Daltons], about 24,000 Daltons [±1,000 Daltons], about 25,000 Daltons [±1,000 Daltons], about 26,000 Daltons [±1,000 Daltons], about 27,000 Daltons [±1,000 Daltons], about 28,000 Daltons [±1,000 Daltons], about 29,000 Daltons [±1,000 Daltons], about 30,000 Daltons [±1,000 Daltons], about 31,000 Daltons [±1,000 Daltons], about 32,000 Daltons [±1,000 Daltons], about 33,000 Daltons [±1,000 Daltons], about 34,000 Daltons [±1,

000 Daltons], or about 35,000 Daltons [±1,000 Daltons]. In additional embodiments, the cross-linkable polycarbonates have a Mw of 17,000 to about 80,000 Daltons. Molecular weight determinations may be performed using gel permeation chromatography (GPC), using a cross-linked styrene-divinylbenzene column and calibrated to polycarbonate references using a UV-VIS detector set at 264 nm, or alternatively using a refractive index detector. Samples may be prepared at a concentration of about 1 mg/ml, and eluted at a flow rate of about 1.0 ml/min.

The cross-linkable polycarbonates of the present disclosure may have a polydispersity index (PDI) of about 2.0 to about 5.0, about 2.0 to about 3.0, or about 2.0 to about 2.5. The PDI is measured prior to any UV exposure.

It is noted that the molecular weight (both weight-average and number-average) of the photoactive additive/cross-linkable polycarbonate can be measured using two different kinds of detectors. More specifically, the molecular weight can be measured using an ultraviolet (UV) detector or using a refractive index (RI) detector, using GPC and calibrated to polycarbonate standards for both detectors.

In embodiments, the ratio of the polydispersity index (PDI) measured using a UV detector to the PDI measured using an RI detector is 1.4 or less, when using a GPC method and polycarbonate molecular weight standards. The ratio may also be 1.2 or less, or 1.1 or less. The PDI ratio has a minimum value of 1.0. As described further herein, the process by which the cross-linkable polycarbonate is made can affect the PDI ratio between the UV detector and the RI detector.

The cross-linkable polycarbonates of the present disclosure may have a melt flow rate (often abbreviated MFR), which measures the rate of extrusion of a composition through an orifice at a prescribed temperature and load. In certain embodiments, the polycarbonates may have an MFR of 1 to 40 grams/10 min, 6 to 15 grams/10 min, 6 to 8 grams/10 min, 6 to 12 grams/10 min, 2 to 30 grams/10 min, 5 to 30 grams/10 min, 8 to 12 grams/10 min, 8 to 10 grams/10 min, or 20 to 30 grams/10 min using the ASTM D1238 method, 1.2 kg load, 300° C. temperature, 360 second dwell.

The cross-linkable polycarbonates of the present disclosure may have a glass transition temperature (Tg) of greater than 120° C., 125° C., 130° C., 135° C., 140° C., 145° C., 150° C., 155° C., 160° C., 165° C., 170° C., 175° C., 180° C., 185° C., 190° C., 200° C., 210° C., 220° C., 230° C., 240° C., 250° C., 260° C., 270° C., 280° C., 290° C., or 300° C., as measured using a differential scanning calorimetry method. In certain embodiments, the polycarbonates have glass transition temperatures ranging from about 120° C. to about 230° C., about 140° C. to about 160° C., about 145° C. to about 155° C., about 148° C. to about 152° C., or about 149° C. to about 151° C.

The cross-linkable polycarbonates of the present disclosure may have a biocontent of 2 wt % to 90 wt %; 5 wt % to 25 wt %; 10 wt % to 30 wt %; 15 wt % to 35 wt %; 20 wt % to 40 wt %; 25 wt % to 45 wt %; 30 wt % to 50 wt %; 35 wt % to 55 wt %; 40 wt % to 60 wt %; 45 wt % to 65 wt %; 55 wt % to 70% wt %; 60 wt % to 75 wt %; 50 wt % to 80 wt %; or 50 wt % to 90 wt %. The biocontent may be measured according to ASTM D6866.

The cross-linkable polycarbonates of the present disclosure may have a modulus of elasticity of greater than or equal to 2200 megapascals (MPa), greater than or equal to 2310 MPa, greater than or equal to 2320 MPa, greater than or equal to 2330 MPa, greater than or equal to 2340 MPa, greater than or equal to 2350 MPa, greater than or equal to 2360 MPa, greater than or equal to 2370 MPa, greater than or equal to 2380 MPa, greater than or equal to 2390 MPa, greater than or

equal to 2400 MPa, greater than or equal to 2420 MPa, greater than or equal to 2440 MPa, greater than or equal to 2460 MPa, greater than or equal to 2480 MPa, greater than or equal to 2500 MPa, or greater than or equal to 2520 MPa as measured by ASTM D 790 at 1.3 mm/min, 50 mm span.

In embodiments, the cross-linkable polycarbonates of the present disclosure may have a flexural modulus of 2,200 to 2,500, preferably 2,250 to 2,450, more preferably 2,300 to 2,400 MPa. In other embodiments, the cross-linkable polycarbonates of the present disclosure may have a flexural modulus of 2,300 to 2,600, preferably 2,400 to 2,600, more preferably 2,450 to 2,550 MPa. The flexural modulus is also measured by ASTM D790.

The cross-linkable polycarbonates of the present disclosure may have a tensile strength at break of greater than or equal to 60 megapascals (MPa), greater than or equal to 61 MPa, greater than or equal to 62 MPa, greater than or equal to 63 MPa, greater than or equal to 64 MPa, greater than or equal to 65 MPa, greater than or equal to 66 MPa, greater than or equal to 67 MPa, greater than or equal to 68 MPa, greater than or equal to 69 MPa, greater than or equal to 70 MPa, greater than or equal to 71 MPa, greater than or equal to 72 MPa, greater than or equal to 73 MPa, greater than or equal to 74 MPa, greater than or equal to 75 MPa as measured by ASTM D 638 Type I at 50 mm/min.

The cross-linkable polycarbonates of the present disclosure may possess a ductility of greater than or equal to 60%, greater than or equal to 65%, greater than or equal to 70%, greater than or equal to 75%, greater than or equal to 80%, greater than or equal to 85%, greater than or equal to 90%, greater than or equal to 95%, or 100% in a notched izod test at −20° C., −15° C., −10° C., 0° C., 5° C., 10° C., 15° C., 20° C., 23° C., 25° C., 30° C., or 35° C. at a thickness of 3.2 mm according to ASTM D 256-10.

The cross-linkable polycarbonates of the present disclosure may have a notched Izod impact strength (NII) of greater than or equal to 500 J/m, greater than or equal to 550 J/m, greater than or equal to 600 J/m, greater than or equal to 650 J/m, greater than or equal to 700 J/m, greater than or equal to 750 J/m, greater than or equal to 800 J/m, greater than or equal to 850 J/m, greater than or equal to 900 J/m, greater than or equal to 950 J/m, or greater than or equal to 1000 J/m, measured at 23° C. according to ASTM D 256.

The cross-linkable polycarbonates of the present disclosure may have a heat distortion temperature of greater than or equal to 110° C., 111° C., 112° C., 113° C., 114° C., 115° C., 116° C., 117° C., 118° C., 119° C., 120° C., 121° C., 122° C., 123° C., 124° C., 125° C., 126° C., 127° C., 128° C., 129° C., 130° C., 131° C., 132° C., 133° C., 134° C., 135° C., 136° C., 137° C., 138° C., 139° C., 140° C., 141° C., 142° C., 143° C., 144° C., 145° C., 146° C., 147° C., 148° C., 149° C., 150° C., 151° C., 152° C., 153° C., 154° C., 155° C., 156° C., 157° C., 158° C., 159° C., 160, 161° C., 162° C., 163° C., 164° C., 165° C., 166° C., 167° C., 168° C., 169° C., or 170° C., as measured according to ASTM D 648 at 1.82 MPa, with 3.2 mm thick unannealed mm bar.

The cross-linkable polycarbonates of the present disclosure may have a percent haze value of less than or equal to 10.0%, less than or equal to 8.0%, less than or equal to 6.0%, less than or equal to 5.0%, less than or equal to 4.0%, less than or equal to 3.0%, less than or equal to 2.0%, less than or equal to 1.5%, less than or equal to 1.0%, or less than or equal to 0.5% as measured at a certain thickness according to ASTM D 1003-07. The polycarbonate haze may be measured at a 2.0, 2.2, 2.4, 2.54, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, or a 4.0 millimeter thickness. The polycarbonate may be measured at a 0.125 inch thickness.

The polycarbonate may have a light transmittance greater than or equal to 50%, greater than or equal to 60%, greater than or equal to 65%, greater than or equal to 70%, greater than or equal to 75%, greater than or equal to 80%, greater than or equal to 85%, greater than or equal to 90%, greater than or equal to 95%, greater than or equal to 96%, greater than or equal to 97%, greater than or equal to 98%, greater than or equal to 99%, greater than or equal to 99.1%, greater than or equal to 99.2%, greater than or equal to 99.3%, greater than or equal to 99.4%, greater than or equal to 99.5%, greater than or equal to 99.6%, greater than or equal to 99.7%, greater than or equal to 99.8%, or greater than or equal to 99.9%, as measured at certain thicknesses according to ASTM D 1003-07. The polycarbonate transparency may be measured at a 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6, 3.8, or a 4.0 millimeter thickness.

In certain embodiments, the cross-linkable polycarbonates of the present disclosure do not include soft block or soft aliphatic segments in the polycarbonate chain. For example, the following aliphatic soft segments that may be excluded from the cross-linkable polycarbonates of the present disclosure include aliphatic polyesters, aliphatic polyethers, aliphatic polythioeithers, aliphatic polyacetals, aliphatic polycarbonates, C—C linked polymers and polysiloxanes. The soft segments of aliphatic polyesters, aliphatic polyethers, aliphatic polythioeithers, aliphatic polyacetals, aliphatic polycarbonates may be characterized as having Number Average MWs (Mns) of greater than 600.

In particular embodiments, the photoactive cross-linkable polycarbonate resin is formed from a dihydroxybenzophenone, a diol chain extender, phosgene, and one or more end-capping agents. Most desirably, the dihydroxybenzophenone is 4,4'-dihydroxybenzophenone. In preferred embodiments, the diol chain extender is bisphenol-A, and the end-capping agent is p-cumylphenol. The resulting photoactive additive (i.e. cross-linkable polycarbonate resin) comprises from about 0.5 mol % to 50 mole % of the dihydroxybenzophenone. In more particular embodiments, the photoactive additive comprises from about 1 wt % to about 5 mole %, or from about 5 wt % to about 20 wt %, or from about 10 wt % to about 20 wt %, of the dihydroxybenzophenone.

In particular embodiments, the cross-linkable polycarbonate is a copolymer consisting of repeating units derived from 4,4'-dihydroxybenzophenone and bisphenol-A, with endcaps that are not photoactive. The copolymer contains from about 0.5 mol % to 25 mole % of the dihydroxybenzophenone, and from about 75 mol % to 99.5 mole % of the bisphenol-A.

Processes

An interfacial polycondensation polymerization process for bisphenol-A (BPA) based polycarbonates can be used to prepare the photoactive additives (PAAs) of the present disclosure. Although the reaction conditions for interfacial polymerization can vary, an exemplary process generally involves dissolving or dispersing one or more dihydric phenol reactants (e.g. the dihydroxybenzophenone, bisphenol-A) in water, adding the resulting mixture to a water-immiscible solvent medium, and contacting the reactants with a carbonate precursor (e.g. phosgene) in the presence of a catalyst (e.g. triethylamine, TEA).

This process typically produces polycarbonates with a polydispersity index (PDI) of less than 3. A higher PDI can indicate an increased low molecular weight fraction in the product. Increased low molecular weight fraction can lead to difficulties in extrusion and injection molding processes by altering the flow behavior or causing the low molecular weight components to volatilize out of the material.

Four different processes are disclosed herein for producing some embodiments of the photoactive additive which contain carbonate linkages. Each process includes the following ingredients: a dihydroxybenzophenone, a diol chain extender, an end-capping agent, a carbonate precursor, a base, a tertiary amine catalyst, water, and a water-immiscible organic solvent, and optionally a branching agent. The dihydroxybenzophenone is the photoactive moiety. It should be noted that more than one of each ingredient can be used to produce the photoactive additive. Some information on each ingredient is first provided below.

The dihydroxybenzophenone is the photoactive moiety previously described. For example, the dihydroxybenzophenone can have the structure of any one of Formulas (16)-(21), or (26)-(29). If desired, more than one dihydroxybenzophenone can be used. In particular embodiments for producing a cross-linkable polycarbonate, the dihydroxybenzophenone is 4,4'-dihydroxybenzophenone of Formula (17).

The diol chain extender may have the structure of any one of Formulas (B)-(I), and include monomers such as bisphenol-A.

The end-capping agent is a monofunctional compound that is not photoactive. Examples of such end-capping agents include phenol, p-cumylphenol (PCP), p-tert-butylphenol, octylphenol, and p-cyanophenol.

The carbonate precursor may be, for example, a carbonyl halide such as carbonyl dibromide or carbonyl dichloride (also known as phosgene), or a haloformate such as a bishaloformate of a dihydric phenol (e.g., the bischloroformate of bisphenol-A, hydroquinone, or the like) or a glycol (e.g., the bishaloformate of ethylene glycol, neopentyl glycol, polyethylene glycol, or the like). Combinations comprising at least one of the foregoing types of carbonate precursors can also be used. In certain embodiments, the carbonate precursor is phosgene, a triphosgene, diacyl halide, dihaloformate, dicyanate, diester, diepoxy, diarylcarbonate, dianhydride, diacid chloride, or any combination thereof. An interfacial polymerization reaction to form carbonate linkages may use phosgene as a carbonate precursor, and is referred to as a phosgenation reaction. Many such carbonate precursors correspond to a structure of Formulas (30, (32), or (33).

The base is used for the regulation of the pH of the reaction mixture. In particular embodiments, the base is an alkali metal hydroxide, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH).

A tertiary amine catalyst is used for polymerization. Exemplary tertiary amine catalysts that can be used are aliphatic tertiary amines such as triethylamine (TEA)), N-ethylpiperidine, 1,4-diazabicyclo[2.2.2]octane (DABCO), tributylamine, cycloaliphatic amines such as N,N-diethyl-cyclohexylamine and aromatic tertiary amines such as N,N-dimethylaniline.

Sometimes, a phase transfer catalyst is also used. Among the phase transfer catalysts that can be used are catalysts of the formula $(R^{30})_4Q^+X$, wherein each R^{30} is the same or different, and is a C_1-C_{10} alkyl group; Q is a nitrogen or phosphorus atom; and X is a halogen atom, C_1-C_8 alkoxy group, or C_6-C_{18} aryloxy group. Exemplary phase transfer catalysts include, for example, $[CH_3(CH_2)_3]_4NX$, $[CH_3(CH_2)_3]_4PX$, $[CH_3(CH_2)_5]_4NX$, $[CH_3(CH_2)_6]_4NX$, $[CH_3(CH_2)_4]_4NX$, $CH_3[CH_3(CH_2)_3]_3NX$, and $CH_3[CH_3(CH_2)_2]_3NX$, wherein X is Cl⁻, Br⁻, a C_1-C_8 alkoxy group or a C_6-C_{18} aryloxy group, such as methyltributylammonium chloride.

The most commonly used water-immiscible solvents include methylene chloride, 1,2-dichloroethane, chlorobenzene, toluene, and the like.

The secondary linker moieties of any one of Formulas (43)-(49) can be used as branching agents.

In the first process, sometimes referred to as the "upfront" process, the dihydroxybenzophenone, diol chain extender, end-capping agent, catalyst, water, and water-immiscible solvent are combined upfront in a vessel to form a reaction mixture. The reaction mixture is then exposed to the carbonate precursor, for example by phosgenation, while the base is co-added to regulate the pH, to obtain the photoactive additive.

To form a cross-linkable polycarbonate using this upfront process, the reaction mixture comprises a dihydroxybenzophenone, a diol chain extender, an end-capping agent, a tertiary amine catalyst, water, and water-immiscible solvent. In more specific embodiments, the dihydroxybenzophenone is 4,4'-dihydroxybenzophenone, the diol chain extender is bisphenol-A, and the water-immiscible solvent is methylene chloride. The phase transfer catalyst, when used, is methyltributylammonium chloride. The end-capping agent may be phenol, p-t-butylphenol, p-cumylphenol, octylphenol, or p-cyanophenol. The pH of the reaction mixture is usually from about 8.5 to about 10, and can be maintained by using a basic solution (e.g. aqueous NaOH). The reaction mixture is then charged with the carbonate precursor, which is usually phosgene. The carbonate precursor is added to the reaction mixture over a period of about 15 minutes to about 45 minutes. While the carbonate precursor is being added, the pH is also maintained in the range of about 8.5 to about 10, again by addition of a basic solution as needed. The cross-linkable polycarbonate is thus obtained, and is then isolated from the reaction mixture.

The resulting photoactive additive (e.g. the cross-linkable polycarbonate) contains only a small amount of low-molecular-weight components. This can be measured in two different ways: the level of diarylcarbonates (DAC) and the lows percentage can be measured. Diarylcarbonates are formed by the reaction of two end-capping agents with phosgene, creating a small molecule that contains no dihydroxybenzophenone or diol chain extender (e.g. bisphenol-A). In embodiments, the resulting photoactive additive contains less than 1000 ppm of diarylcarbonates. The lows percentage is the percentage by weight of oligomeric chains having a molecular weight of less than 1000. In embodiments, the lows percentage is 2.0 wt % or less, including from about 1.0 wt % to 2.0 wt %. The DAC level and the lows percentage can be measured by high performance liquid chromatography (HPLC) or gel permeation chromatography (GPC). Also of note is that the resulting photoactive additive does not contain any residual pyridine, because pyridine is not used in the manufacture of the photoactive additive.

In the second process, also known as the "solution addition" process, the dihydroxybenzophenone, diol chain extender, tertiary amine catalyst, water, and water-immiscible solvent are combined in a vessel to form a reaction mixture. The total charge of the carbonate precursor is then added to this reaction mixture in the vessel over a total time period, while the base is co-added to regulate the pH. The carbonate precursor is first added to the reaction mixture along with the base to regulate the pH for a first time period. After the first time period ends, the end-capping agent is added in a controlled manner to the reaction mixture, also referred to as programmed addition. The addition of the end-capping agent occurs for a second time period after the first time period, rather than as a bolus at the beginning of the reaction (as in the upfront process). The carbonate precursor and the base are also added concurrently with the end-capping agent during the second time period. After the second

time period ends, the remainder of the carbonate precursor continues uninterrupted for a third time period until the total charge is reached. The base is also co-added during the third time period to regulate the reaction pH. The end-capping agent is not added during either the first time period or the third time period. The photoactive additive is thus obtained. The first and second processes are illustrated in FIG. **4** using 4,4'-hydroxybenzophenone, bisphenol-A, p-cumylphenol, and phosgene. The main difference is in the addition of the end-capping agent over time.

To form a cross-linkable polycarbonate using this solution addition process, the reaction mixture comprises the dihydroxybenzophenone, diol chain extender, tertiary amine catalyst, water, and water-immiscible solvent. In more specific embodiments, the dihydroxybenzophenone is 4,4'-hydroxybenzophenone, the diol chain extender is bisphenol-A, and the water-immiscible solvent is methylene chloride. The pH of the reaction mixture is usually from about 8.5 to about 10, and can be maintained by using a basic solution (e.g. aqueous NaOH, made from the base).

The end-capping agent can be phenol, p-t-butylphenol, p-cumylphenol, octylphenol, or p-cyanophenol. The end-capping agent is separately dissolved in a solvent to form a solution which is then added to the reaction mixture. The solvent in this solution can be the same as the water-immiscible solvent (e.g. methylene chloride). Alternatively, the solvent can be water that contains a base, so that the solution is a dilute aqueous basic solution. The base may be, for example, NaOH, or other similar bases. In embodiments, the dilute aqueous basic solution contains from about 1 to about 2 moles of the base per mole of the end-capping agent, and contains from about 5 wt % to about 20 wt % of the end-capping agent.

The reaction mixture is then charged with the carbonate precursor, which is usually phosgene. The carbonate precursor is added to the reaction mixture over a total time period, which may be for example from about 15 minutes to about 45 minutes. The total time period is the duration needed to add the total charge of the carbonate precursor (measured either by weight or by moles) to the reaction mixture. While the carbonate precursor is being added, the pH is also maintained in the range of about 8.5 to about 10, again by addition of a basic solution as needed. It is contemplated that the carbonate precursor is added at a constant rate over the total time period.

The carbonate precursor is first added to the reaction mixture along with the base to regulate the pH for a first time period, ranging from about 2 minutes to about 20 minutes. Then, during a second time period, the solution containing the end-capping agent is added to the reaction mixture concurrently with the carbonate precursor and the base. It is contemplated that the end-capping agent is added at a constant rate during this second time period, which can range from about 1 minute to about 5 minutes. After the second time period ends, the remaining carbonate precursor is charged to the reaction mixture for a third time period, along with the base to regulate the reaction pH. The cross-linkable polycarbonate is thus obtained, and is then isolated from the reaction mixture.

The total time period for the reaction is the sum of the first time period, the second time period, and the third time period. In particular embodiments, the second time period in which the solution containing the end-capping agent is added to the reaction mixture begins at a point between 10% to about 40% of the total time period. Put another way, the first time period is 10% of the total time period.

For example, if 2400 grams of phosgene were to be added to a reaction mixture at a rate of 80 g/min, and 500 ml of a PCP solution were to be added to the reaction mixture at a rate of 500 ml/min after an initial charge of 240 grams of phosgene, then the total time period would be 30 minutes, the first time period would be three minutes, the second time period would be one minute, and the third period would be 26 minutes.

Again, the resulting photoactive additive (e.g. the cross-linkable polycarbonate) contains only a small amount of low-molecular-weight components. In embodiments, the lows percentage can be 2 wt % or less, including from about 1.0 wt % to 1.5 wt %. Again, the resulting photoactive additive does not contain any residual pyridine.

The third process is also referred to as a bis-chloroformate or chloroformate (BCF) process. Chloroformate oligomers are prepared by reacting the carbonate precursor, specifically phosgene, with the dihydroxybenzophenone and the diol chain extender in the absence of the tertiary amine catalyst, while the base is co-added to regulate the pH. The chloroformate oligomers can contain a mixture of monochloroformates, bischloroformates, and bisphenol terminated oligomers. After the chloroformate oligomers are generated, the phosgene can optionally be allowed to substantially condense or hydrolyze, then the end-capping agent is added to the chloroformate mixture. The reaction is allowed to proceed, and the tertiary amine catalyst is added to complete the reaction. This process is illustrated in FIG. **5**.

To form a cross-linkable polycarbonate using the BCF addition process, the reaction mixture comprises the dihydroxybenzophenone, diol chain extender, water, and water-immiscible solvent. In more specific embodiments, the dihydroxybenzophenone is 4,4'-dihydroxybenzophenone, the carbonate precursor is phosgene, the diol chain extender is bisphenol-A, and water-immiscible solvent is methylene chloride. The end-capping agent can be phenol, p-t-butylphenol, p-cumylphenol, octylphenol, or p-cyanophenol. The pH of the reaction mixture is usually from about 8.5 to about 10 prior to the addition of the phosgene. During the addition of the phosgene, the pH is maintained between about 6 and about 8, by using a basic solution (e.g. aqueous NaOH).

The end-capping agent can be dissolved in a solvent to form a solution which is then added to the reaction mixture. Again, the solvent in this solution can be the same as the water-immiscible solvent (e.g. methylene chloride), or can be a dilute aqueous basic solution as described above. The solution containing the end-capping agent is added to the reaction mixture and allowed to react. Next, a solution containing the tertiary amine catalyst is added to the reaction mixture, which catalyzes the polymerization.

The resulting photoactive additive (e.g. the cross-linkable polycarbonate) contains only a small amount of low-molecular-weight components. In embodiments, the lows percentage can be 2.0 wt % or less, including from about 1.0 wt % to 1.5 wt %. Again, the resulting photoactive additive does not contain any residual pyridine.

The fourth process uses a tubular reactor. In the tubular reactor, the end-capping agent is pre-reacted with the carbonate precursor (specifically phosgene) to form chloroformates. The water-immiscible solvent is used as a solvent in the tubular reactor. In a separate reactor, the dihydroxybenzophenone, diol chain extender, tertiary amine catalyst, water, and water-immiscible solvent are combined to form a reaction mixture. The chloroformates in the tubular reactor are then fed into the reactor over a first time period along with additional carbonate precursor to complete the reaction while the base is co-added to regulate the pH. This process is illustrated in FIG. **6** using p-cumylphenol as the end-capping agent.

To form a cross-linkable polycarbonate using the tubular reactor process, the reaction mixture comprises the dihy-

droxybenzophenone, diol chain extender, tertiary amine catalyst, water, and water-immiscible solvent. In more specific embodiments, the dihydroxybenzophenone is 4,4'-dihydroxybenzophenone, the diol chain extender is bisphenol-A, the tertiary amine catalyst is triethylamine, and the water-immiscible solvent is methylene chloride. In the tubular reactor, the end-capping agent is pre-reacted with phosgene. The end-capping agent can be phenol, p-t-butylphenol, p-cumylphenol, octylphenol, or p-cyanophenol. The pH of the reaction mixture is usually from about 8.5 to about 10 prior to the addition of the chloroformates. During the addition of the chloroformates, the pH is maintained between about 8.5 and about 10, by using a basic solution (e.g. aqueous NaOH).

The resulting photoactive additive (e.g. the cross-linkable polycarbonate) contains only a small amount of low-molecular-weight components. In embodiments, the lows percentage can be 2.0 wt % or less. Again, the resulting photoactive additive does not contain any residual pyridine.

The additives, when used, can improve the chemical resistance of the final product. It is contemplated that products can be of any desired shape (e.g. molded article, film, sheet, etc.) and be used in many different applications, for example in the medical, automotive, and consumer electronics fields. Increased chemical resistance may be found against 409 Glass and Surface Cleaner; Alcohol Prep Pad; CaviCide liquid/CaviWipes; CaviWipes; Cidex Plus liquid; Clorox Bleach; Clorox Wipes; Envirocide liquid; For Pro liquid; Gentle dish soap and water; Hydrogen Peroxide Cleaner Disinfectant Wipes; Isopropyl Alcohol wipes; MadaCide-1 liquid; Mar-V-Cide liquid to dilute; Sani-Cloth Bleach Wipes; Sani-Cloth HB Wipes; Sani-Cloth Plus Wipes; Sodium Hypochlorite liquid; Super Sani-Cloth Wipes; Viraguard liquid and Wipes; Virex 256; Windex Blue; Fuel C; Toluene; Heptane; Ethanol; Isopropanol; Windex; Engine oil; WD40; Transmission fluid; Break fluid; Glass wash; Diesel; Gasoline; Banana Boat Sunscreen (SPF 30); Sebum; Ivory Dish Soap; SC Johnson Fantastik Cleaner; French's Yellow Mustard; Coca-Cola; 70% Isopropyl Alcohol; Extra Virgin Olive Oil; Vaseline Intensive Care Hand Lotion; Heinz Ketchup; Kraft Mayonnaise; Chlorox Formula 409 Cleaner; SC Johnson Windex Cleaner with Ammonia; Acetone; Artificial Sweat; Fruits & Passion Cucina Coriander & Olive Hand Cream; Loreal Studioline Megagel Hair Gel; Maybelline Lip Polish; Maybelline Expert Wear Blush—Beach Plum Rouge; Purell Hand Sanitizer; Hot coffee, black; iKlear; Chlorox Wipes; Squalene; Palmitic Acid; Oleic Acid; Palmitoleic Acid; Stearic Acid; and Olive Oil.

Second Polymer Resin

The PAAs are suitable for blending with a variety of resins. Such blends can still be sufficiently cross-linked to provide compositions that exhibit one or more of UL94 5VA compliance, extreme chemical resistance, tear resistance, impact strength, ductility, hydrolytic stability, and weatherability. The PAAs are suitable for blending with polycarbonate homopolymers, polycarbonate copolymers, and polycarbonate blends. They are also suitable for blending with polyesters, polyarylates, polyestercarbonates, and polyetherimides. One advantage of using the PAAs with polymeric resins is that polymers with relatively higher Mw's generally retain their mechanical properties better, while polymers with relatively lower Mw's generally have better flow properties. The PAAs can be used to produce complex or thin products that are difficult to mold using higher molecular weight polymers.

Upon irradiation of the product, crosslinks can be formed that extend the molecular weight and improve physical properties such as impact strength, tensile strength, flame retardance, or chemical resistance.

UV Irradiation

The photoactive additive (PAA) can be blended with one or more polymeric base resins by melt blending or solution blending to form a polymeric composition/blend. The PAA-containing blend can be then be formed into a product by a variety of known processes such as solution casting, profile extrusion, film and/or sheet extrusion, sheet-foam extrusion, injection molding, blow molding, thermoforming, and the like. The product is then exposed to ultraviolet (UV) light at an appropriate wavelength and in an appropriate dosage that brings about the desired amount of crosslinking for the given application. Depending on the end use application and the desired properties, the UV exposure can be performed on one or more surfaces of the product.

The product where the enhanced properties are needed should be exposed with a substantially uniform dose of UV light. The exposure can be accomplished using standard methods known in the art. For example, the UV light can come from any source of UV light such as, but not limited to, those lamps powered by microwave, HID lamps, and mercury vapor lamps. In some other embodiments, the product is exposed by using natural sunlight. The exposure time will be dependent on the application and color of material. It can range from a few minutes to several days. Alternatively, the crosslinking can be accomplished by using a UV-emitting light source such as a mercury vapor, High-Intensity Discharge (HID), or various UV lamps. For example, commercial UV lamps are sold for UV curing from manufacturers such as Hereaus Noblelight Fusion UV. Non-limiting examples of UV-emitting light bulbs include mercury bulbs (H bulbs), or metal halide doped mercury bulbs (D bulbs, H+ bulbs, and V bulbs). Other combinations of metal halides to create a UV light source are also contemplated. Exemplary bulbs could also be produced by assembling the lamp out of UV-absorbing materials and considered as a filtered UV source. An undoped mercury arc lamp is not used for irradiation. An H bulb has strong output in the range of 200 nm to 320 nm. The D bulb has strong output in the 320 nm to 400 nm range. The V bulb has strong output in the 400 nm to 420 nm range.

It may also be advantageous to use a UV light source where the harmful wavelengths (those that cause polymer degradation or excessive yellowing) are removed or not present. Equipment suppliers such as Heraeus Noblelight Fusion UV provide lamps with various spectral distributions. The light can also be filtered to remove harmful or unwanted wavelengths of light. This can be done with optical filters that are used to selectively transmit or reject a wavelength or range of wavelengths. These filters are commercially available from a variety of companies such as Edmund Optics or Praezisions Glas & Optik GmbH. Bandpass filters are designed to transmit a portion of the spectrum, while rejecting all other wavelengths. Longpass edge filters are designed to transmit wavelengths greater than the cut-on wavelength of the filter. Shortpass edge filters are used to transmit wavelengths shorter than the cut-off wavelength of the filter. Various types of materials, such as borosilicate glass, can be used as a long pass filter. Schott and/or Praezisions Glas & Optik GmbH for example have the following long pass filters: WG225, WG280, WG295, WG305, WG320 which have cut-on wavelengths of ~225, 280, 295, 305, and 320 nm, respectively.

These filters can be used to screen out the harmful short wavelengths while transmitting the appropriate wavelengths for the crosslinking reaction.

The exposed product will have a cross-linked outer surface and an inner surface that is either lightly cross-linked or not cross-linked. The outer surface can be cross-linked to such a degree that the outer surface is substantially insoluble in the common solvents for the starting resins. The percentage of the insolubles (insoluble component) will be dependent on the part geometry and surface-to-volume ratio.

The compositions disclosed herein are useful in the manufacture of a wide variety of articles, particularly thin-walled articles, including highly transparent thin-walled articles, having improved flame retardance and good physical properties. The compositions can be used to provide materials and articles such as, but not limited to, injection molded articles, films, extruded sheets, fibers, pellets, flex-films, tear-resistant films, and PVD laminates.

The present disclosure has multiple aspects, illustrated by the following non-limiting examples.

EXAMPLES

Methods

All solvents and reagents used were analytical grade.

Molecular weight determinations were performed using gel permeation chromatography (GPC), using a cross-linked styrene-divinylbenzene column and calibrated to polycarbonate references using a UV-VIS detector set at 264 nm. Samples were prepared at a concentration of about 1 mg/ml, and eluted at a flow rate of about 1.0 ml/min. Optionally, a refractive index (RI) detector can be used.

Differential scanning calorimetry (DSC) employing a temperature sweep rate of 20° C./min was used to determine glass transition temperatures of polycarbonates.

Flammability testing was conducted using the standard Underwriters Laboratory UL 94 test method (2 day or 7 day conditioning), except that 20 bars rather than the usual 5 bars were tested. Specimens are to be preconditioned either at room temperature for 48 hours or in an air-circulating oven for 168 hours at 70±1° C. and then cooled in a desiccator for at least 4 hours at room temperature, prior to testing. Once removed from the desiccator, specimens are tested within 30 minutes.

Flammability tests were performed following the procedure of Underwriter's Laboratory Bulletin 94 entitled "Tests for Flammability of Plastic Materials, UL94". Several ratings can be applied based on the rate of burning, time to extinguish, ability to resist dripping, and whether or not drips are burning. According to this procedure, materials may be classified as HB, V0, V1, V2, 5V, 5VA and/or 5VB on the basis of the test results obtained for five samples. The criteria for the flammability classifications or "flame retardance" are described below.

V0: A specimen is supported in a vertical position and a flame is applied to the bottom of the specimen. The flame is applied for ten seconds and then removed until flaming stops at which time the flame is reapplied for another ten seconds and then removed. Two sets of five specimens are tested. The two sets are conditioned under different conditions.

To achieve a V0 rating, specimens must not burn with flaming combustion for more than 10 seconds after either test flame application. Total flaming combustion time must not exceed 50 seconds for each set of 5 specimens. Specimens must not burn with flaming or glowing combustion up to the specimen holding clamp. Specimens must not drip flaming

particles that ignite the cotton. No specimen can have glowing combustion remain for longer than 30 seconds after removal of the test flame

5VA: Testing is done on both bar and plaque specimens. Procedure for Bars: A bar specimen is supported in a vertical position and a flame is applied to one of the lower corners of the specimen at a 20° angle. The flame is applied for 5 seconds and is removed for 5 seconds. The flame application and removal is repeated five times. Procedure for Plaques: The procedure for plaques is the same as for bars except that the plaque specimen is mounted horizontally and a flame is applied to the center of the lower surface of the plaque.

To achieve a 5VA rating, specimens must not have any flaming or glowing combustion for more than 60 seconds after the five flame applications. Specimens must not drip flaming particles that ignite the cotton. Plaque specimens must not exhibit burnthrough (a hole). It is noted that in the Examples and Tables below, the rows that state whether 5VA was "Pass" or "Fail" for a given thickness refer only to whether the plaque test was passed, and should not be interpreted as stating that no combustion occurred for more than 60 seconds and that there were no drips. Results for both 2-day and 7-day conditioning are reported.

The data was analyzed by calculation of the average flame out time, standard deviation of the flame out time and the total number of drips. Statistical methods were used to convert the data to a probability that a specific formulation would achieve a first time V0 pass or "p(FTP)" in the standard UL 94 testing of 5 bars. The probability of a first time pass on a first submission (pFTP) may be determined according to the formula:

$$pFTP = (P_{t1>mbt,n=0} \times P_{t2>mbt,n=0} \times P_{total<=mtbt} \times P_{drip,n=0})$$

where $P_{t1>mbt,n=0}$ is the probability that no first burn time exceeds a maximum burn time value, $P_{t2>mbt,n=0}$ is the probability that no second burn time exceeds a maximum burn time value, $P_{total<=mtbt}$ is the probability that the sum of the burn times is less than or equal to a maximum total burn time value, and $P_{drip,n=0}$ is the probability that no specimen exhibits dripping during the flame test. First and second burn time refer to burn times after a first and second application of the flame, respectively.

The probability that no first burn time exceeds a maximum burn time value, $P_{t1>mbt,n=0}$, may be determined from the formula: $P_{t1>mbt,n=0} = (1-P_{t1>mbt})^5$ where $P_{t1>mbt}$ is the area under the log normal distribution curve for t1>mbt, and where the exponent "5" relates to the number of bars tested. The probability that no second burn time exceeds a maximum burn time value may be determined from the formula: $P_{t2>mbt,n=0} = (1-P_{t2>mbt})$ where $P_{t2>mbt}$ is the area under the normal distribution curve for t2>mbt. As above, the mean and standard deviation of the burn time data set are used to calculate the normal distribution curve. For the UL-94 V-0 rating, the maximum burn time is 10 seconds. For a V-1 or V-2 rating the maximum burn time is 30 seconds. The probability $P_{drip,n=0}$ that no specimen exhibits dripping during the flame test is an attribute function, estimated by: $(1-P_{drip})^5$ where $P_{drip} = $ (the number of bars that drip/the number of bars tested).

The probability $P_{total<=mtbt}$ that the sum of the burn times is less than or equal to a maximum total burn time value may be determined from a normal distribution curve of simulated 5-bar total burn times. The distribution may be generated from a Monte Carlo simulation of 1000 sets of five bars using the distribution for the burn time data determined above. Techniques for Monte Carlo simulation are well known in the art. A normal distribution curve for 5-bar total burn times may be generated using the mean and standard deviation of the simulated 1000 sets. Therefore, $P_{total<=mtbt}$ may be deter-

mined from the area under a log normal distribution curve of a set of 1000 Monte Carlo simulated 5-bar total burn time for total<=maximum total burn time. For the UL94 V0 rating, the maximum total burn time is 50 seconds. For a V1 rating, the maximum total burn time is 250 seconds.

Preferably p(FTP) values will be 1 or very close to 1 for high confidence that a sample formulation would achieve a V0 rating in UL 94 testing.

Cross-linked polycarbonate samples were evaluated for chemical resistance under strain conditions. A tensile bar was positioned in a strain jig, so that the curvature of the jig induced a 0.5% or 1% stress level on the tensile bar. A portion of the bar was exposed to a solvent by dripping the solvent on top of the tensile bars. The bar was then allowed to sit on the jig for 24 hours, during which time the solvent evaporated. The % elongation at break was then reported.

Samples were sometimes exposed to various doses of either filtered or unfiltered UV light. The unfiltered light was provided by a Fusion UV system, which used a D-bulb elec-trodeless bulb. The filtered light was provided by a Loctite Zeta 7411-S system, which used a 400W metal halide arc lamp and behaved like a D-bulb electrodeless bulb in spectral output with a 280-nm cut-on wavelength filter. The samples were exposed on both sides beneath the UV lights for the equivalent UVA dosage of 12, 36, or 60 J/cm^2 per side. The UV energy (per pass or dose) for each system is provided below in Table A and Table B, and was measured using an EIT PowerPuck. The dose was measured as the energy from 320-390 nm (UVA), 280-320 nm (UVB), 250-260 nm (UVC) and 395-445 nm (UVV). The dose was calculated in J/cm^2.

TABLE A

Loctite (filtered light).			
	Loctite Dose		
Filtered	UVA J/cm^2	UVB J/cm^2	UVC J/cm^2	UVV J/cm^2
320 sec exposure	12.0	2.4	0	7.3
960 sec exposure	36.0	7.2	0	21.9
1600 sec exposure	60.2	12.1	0	36.6

TABLE B

Fusion (unfiltered light)			
	Fusion UV		
Unfiltered	UVA J/cm^2	UVB J/cm^2	UVC J/cm^2	UVV J/cm^2
2 passes	12.0	3.7	0.45	5.8
6 passes	35.9	11.0	1.34	17.5
10 passes	59.9	18.3	2.24	29.2

The various examples may contain the components shown in Table C.

TABLE C

Component	Description	Trade name, Source
Rimar Salt	Potassium perfluorobutanesulfonate	Lanxess
Phosphite Stabilizer	Tris (2,4-di-tert-butylphenyl) phosphite	Irgaphos 168

Example 1

(A) Preparation of Cross-Linkable Polycarbonates

(i) Solution Addition

Sample A1

Sample A1 was made using solution program addition to obtain a crosslinkable polycarbonate resin containing 1.6 mole % of 4,4'-dihydroxybenzophenone (DHBP).

A solution of p-cumylphenol (193 grams, 0.91 moles, 4.4 mole %) was prepared in 500 mL of dichloromethane. The p-cumylphenol (PCP) solution was placed in an addition pot connected to the reactor via a dosing pump.

To the formulation tank was added dichloromethane (13 L), DI water (10 L), 4,4'-dihydroxybenzophenone (70 grams, 0.33 moles, 1.6 mole %), bisphenol-A (4430 grams, 19.4 moles), triethylamine (52 grams, 0.37 moles) and sodium gluconate (10 grams, iron scavenger). The mixture was stirred for 5 minutes, then transferred to the 70 L batch reactor which was equipped with an overhead condenser, circulation loop, pH probe and various material addition nozzles. The formulation tank was rinsed with dichloromethane (8 L) which was transferred to the batch reactor. The reactor agita-tor was started and the circulation flow was set at 80 L/min. Phosgene vapor flow to the reactor was initiated (80 g/min flow rate) by the digital control system (DCS) and an initial amount (240 grams, 2.4 moles) was added. The pH of the reaction was maintained at a target of 10.0 by DCS-controlled addition of 33% aqueous NaOH.

After addition of the initial amount of phosgene, the PCP solution was added to the reactor at 500 mL/min flow rate by DCS control while phosgene flow to the reactor continued (i.e. all PCP added in one minute). Phosgene addition contin-ued until the total set point was reached (2400 grams, 24.3 moles, 30 minutes total reaction time). After completion of the phosgene addition, a sample of the reactor was obtained and verified to be free of un-reacted BPA and free of chloro-formate. Mw of a reaction sample was determined by GPC using a UV detector (Mw=21604, PDI=2.4). An additional charge of phosgene was added (200 grams, 2.0 mole) to the reactor. The reactor was purged with nitrogen then the batch was transferred to the centrifuge feed tank.

To the batch in the centrifuge feed tank was added dilution dichloromethane (8 L) then the mixture was purified using a train of liquid-liquid centrifuges. Centrifuge one separated the brine phase. Centrifuge two removed the triethylamine catalyst by extracting the resin solution with aqueous hydro-chloric acid (pH 1). Centrifuges three through eight removed residual ions by extracting the resin solution with DI water. A sample of the resin solution was tested and verified less than 5 ppm each of ionic chloride and residual triethylamine.

The resin solution was transferred to the precipitation feed tank. The resin was isolated as a white powder by steam precipitation followed by drying in a cone shaped vessel using heated nitrogen (210 F). Powder yield 3855 grams. Mw=21536 PDI=2.3.

Sample A2

Sample A2 was made using solution program addition to obtain a crosslinkable polycarbonate resin containing 5.1 mole % of 4,4'-dihydroxybenzophenone (DHBP).

A solution of p-cumylphenol (196 grams, 0.92 moles, 4.5 mole %) was prepared in 500 mL of dichloromethane. The p-cumylphenol (PCP) solution was placed in an addition pot connected to the reactor via a dosing pump.

To the formulation tank was added dichloromethane (13 L), DI water (10 L), 4,4'-dihydroxybenzophenone (225 grams, 1.1 moles, 5.1 mole %), bisphenol-A (4275 grams, 18.7 moles), triethylamine (52 grams, 0.37 moles) and

sodium gluconate (10 grams, iron scavenger). The mixture was stirred for 5 minutes, then transferred to the 70 L batch reactor which was equipped with an overhead condenser, circulation loop, pH probe and various material addition nozzles. The formulation tank was rinsed with dichloromethane (8 L) which was transferred to the batch reactor. The reactor agitator was started and the circulation flow was set at 80 L/min. Phosgene vapor flow to the reactor was initiated (80 g/min flow rate) by the DCS and an initial amount (240 grams, 2.4 moles) was added. The pH of the reaction was maintained at a target of 10.0 by DCS-controlled addition of 33% aqueous NaOH.

After addition of the initial amount of phosgene, the PCP solution was added to the reactor at 500 mL/min flow rate by DCS control while phosgene flow to the reactor continued. Phosgene addition continued until the total set point was reached (2400 grams, 24.3 moles). After completion of the phosgene addition, a sample of the reactor was obtained and verified to be free of un-reacted BPA and free of chloroformate. Mw of a reaction sample was determined by GPC using a UV detector (Mw=21761, PDI=2.3). An additional charge of phosgene was added (200 grams, 2.0 mole) to the reactor. The reactor was purged with nitrogen then the batch was transferred to the centrifuge feed tank.

To the batch in the centrifuge feed tank was added dilution dichloromethane (8 L) then the mixture was purified using a train of liquid-liquid centrifuges. Centrifuge one separated the brine phase. Centrifuge two removed the triethylamine catalyst by extracting the resin solution with aqueous hydrochloric acid (pH 1). Centrifuges three through eight removed residual ions by extracting the resin solution with DI water. A sample of the resin solution was tested and verified less than 5 ppm each of ionic chloride and residual triethylamine.

The resin solution was transferred to the precipitation feed tank. The resin was isolated as a white powder by steam precipitation followed by drying in a cone shaped vessel using heated nitrogen (210 F). Powder yield 3995 grams. Mw=21454 PDI=2.2.

Sample A3

Sample A3 was made using solution program addition to obtain a crosslinkable polycarbonate resin containing 10.1 mole % of 4,4'-dihydroxybenzophenone (DHBP).

A solution of p-cumylphenol (198 grams, 0.93 moles, 4.5 mole %) was prepared in 500 mL of dichloromethane. The p-cumylphenol (PCP) solution was placed in an addition pot connected to the reactor via a dosing pump.

To the formulation tank was added dichloromethane (13 L), DI water (10 L), 4,4'-dihydroxybenzophenone (450 grams, 2.1 moles, 10.1 mole %), bisphenol-A (4050 grams, 17.7 moles), triethylamine (52 grams, 0.37 moles) and sodium gluconate (10 grams, iron scavenger). The mixture was stirred for 5 minutes, then transferred to the 70 L batch reactor which was equipped with an overhead condenser, circulation loop, pH probe and various material addition nozzles. The formulation tank was rinsed with dichloromethane (8 L) which was transferred to the batch reactor. The reactor agitator was started and the circulation flow was set at 80 L/min. Phosgene vapor flow to the reactor was initiated (80 g/min flow rate) by the DCS and an initial amount (240 grams, 2.4 moles) was added. The pH of the reaction was maintained at a target of 10.0 by DCS-controlled addition of 33% aqueous NaOH.

After addition of the initial amount of phosgene, the PCP solution was added to the reactor at 500 mL/min flow rate by DCS control while phosgene flow to the reactor continued. Phosgene addition continued until the total set point was reached (2400 grams, 24.3 moles). After completion of the

phosgene addition, a sample of the reactor was obtained and verified to be free of un-reacted BPA and free of chloroformate. Mw of a reaction sample was determined by GPC using a UV detector (Mw=21732, PDI=2.3). An additional charge of phosgene was added (200 grams, 2.0 mole) to the reactor. The reactor was purged with nitrogen then the batch was transferred to the centrifuge feed tank.

To the batch in the centrifuge feed tank was added dilution dichloromethane (8 L) then the mixture was purified using a train of liquid-liquid centrifuges. Centrifuge one separated the brine phase. Centrifuge two removed the triethylamine catalyst by extracting the resin solution with aqueous hydrochloric acid (pH 1). Centrifuges three through eight removed residual ions by extracting the resin solution with DI water. A sample of the resin solution was tested and verified less than 5 ppm each of ionic chloride and residual triethylamine.

The resin solution was transferred to the precipitation feed tank. The resin was isolated as a white powder by steam precipitation followed by drying in a cone shaped vessel using heated nitrogen (210 F). Powder yield 4040 grams. Mw=21523 PDI=2.2.

Sample A4

Sample A4 was made using solution program addition to obtain a crosslinkable polycarbonate resin containing 20.1 mole % of 4,4'-dihydroxybenzophenone (DHBP).

A solution of p-cumylphenol (202 grams, 0.95 moles, 4.5 mole %) was prepared in 500 mL of dichloromethane. The p-cumylphenol (PCP) solution was placed in an addition pot connected to the reactor via a dosing pump.

To the formulation tank was added dichloromethane (13 L), DI water (10 L), 4,4'-dihydroxybenzophenone (900 grams, 4.2 moles, 20.1 mole %), bisphenol-A (3600 grams, 15.8 moles), triethylamine (52 grams, 0.37 moles) and sodium gluconate (10 grams, iron scavenger). The mixture was stirred for 5 minutes, then transferred to the 70 L batch reactor which was equipped with an overhead condenser, circulation loop, pH probe and various material addition nozzles. The formulation tank was rinsed with dichloromethane (8 L) which was transferred to the batch reactor. The reactor agitator was started and the circulation flow was set at 80 L/min. Phosgene vapor flow to the reactor was initiated (80 g/min flow rate) by the DCS and an initial amount (240 grams, 2.4 moles) was added. The pH of the reaction was maintained at a target of 10.0 by DCS-controlled addition of 33% aqueous NaOH.

After addition of the initial amount of phosgene, the PCP solution was added to the reactor at 500 mL/min flow rate by DCS control while phosgene flow to the reactor continued. Phosgene addition continued until the total set point was reached (2400 grams, 24.3 moles). After completion of the phosgene addition, a sample of the reactor was obtained and verified to be free of un-reacted BPA and free of chloroformate. Mw of a reaction sample was determined by GPC using a UV detector (Mw=21732, PDI=2.2). An additional charge of phosgene was added (200 grams, 2.0 mole) to the reactor. The reactor was purged with nitrogen then the batch was transferred to the centrifuge feed tank.

To the batch in the centrifuge feed tank was added dilution dichloromethane (8 L) then the mixture was purified using a train of liquid-liquid centrifuges. Centrifuge one separated the brine phase. Centrifuge two removed the triethylamine catalyst by extracting the resin solution with aqueous hydrochloric acid (pH 1). Centrifuges three through eight removed residual ions by extracting the resin solution with DI water. A sample of the resin solution was tested and verified less than 5 ppm each of ionic chloride and residual triethylamine.

The resin solution was transferred to the precipitation feed tank. The resin was isolated as a white powder by steam precipitation followed by drying in a cone shaped vessel using heated nitrogen (210 F). Powder yield 3314 grams. Mw=21401 PDI=2.1.

Sample A7

Sample A7 was made using solution program addition to obtain a crosslinkable polycarbonate resin containing 1.5 mole % of 4,4'-dihydroxybenzophenone (DHBP).

A solution of p-tert-butylphenol (76.5 grams, 0.51 mole, 2.5 mole %) was prepared in 500 mL of dichloromethane. The p-tert-butylphenol (PTBP) solution was placed in an addition pot connected to the reactor via a dosing pump.

To the formulation tank was added dichloromethane (10 L), DI water (10 L), 4,4'-dihydroxybenzophenone (65 grams, 0.30 moles, 1.5 mole %), bisphenol-A (4435 grams, 19.4 moles), triethylamine (52 grams, 0.37 moles) and sodium gluconate (10 grams, iron scavenger). The mixture was stirred for 5 minutes, then transferred to the 70 L batch reactor which was equipped with an overhead condenser, circulation loop, pH probe and various material addition nozzles. The formulation tank was rinsed with dichloromethane (8 L) which was transferred to the batch reactor. The reactor agitator was started and the circulation flow was set at 80 L/min. Phosgene vapor flow to the reactor was initiated (80 g/min flow rate) by the DCS and an initial amount (240 grams, 2.4 moles) was added. The pH of the reaction was maintained at a target of 10.0 by DCS-controlled addition of 33% aqueous NaOH.

After addition of the initial amount of phosgene, the PCP solution was added to the reactor at 500 mL/min flow rate by DCS control while phosgene flow to the reactor continued. Phosgene addition continued until the total set point was reached (2400 grams, 24.3 moles). After completion of the phosgene addition, a sample of the reactor was obtained and verified to be free of un-reacted BPA and free of chloroformate. Mw of a reaction sample was determined by GPC using a UV detector (Mw=35969, PDI=4.8). An additional charge of phosgene was added (200 grams, 2.0 mole) to the reactor. The total amount of excess phosgene was 21%. The reactor was purged with nitrogen then the batch was transferred to the centrifuge feed tank.

To the batch in the centrifuge feed tank was added dilution dichloromethane (8 L) then the mixture was purified using a train of liquid-liquid centrifuges. Centrifuge one separated the brine phase. Centrifuge two removed the triethylamine catalyst by extracting the resin solution with aqueous hydrochloric acid (pH 1). Centrifuges three through eight removed residual ions by extracting the resin solution with DI water. A sample of the resin solution was tested and verified less than 5 ppm each of ionic chloride and residual triethylamine.

The resin solution was transferred to the precipitation feed tank. The resin was isolated as a white powder by steam precipitation followed by drying in a cone shaped vessel using heated nitrogen (210 F). Powder yield 3493 grams. Mw=35935 PDI=3.2.

Sample A8

Sample A8 was made according to the same procedure as Sample A7.

Sample A5

Sample A5 was made using solution program addition to obtain a crosslinkable polycarbonate resin containing 1.5 mole % of 4,4'-dihydroxybenzophenone (DHBP).

A solution of p-cumylphenol (108 grams, 0.51 mole, 2.5 mole %) was prepared in 500 mL of dichloromethane. The p-cumyl (PCP) solution was placed in an addition pot connected to the reactor via a dosing pump.

To the formulation tank was added dichloromethane (10 L), DI water (10 L), 4,4'-dihydroxybenzophenone (65 grams, 0.30 moles, 1.5 mole %), bisphenol-A (4435 grams, 19.4 moles), triethylamine (52 grams, 0.37 moles) and sodium gluconate (10 grams, iron scavenger). The mixture was stirred for 5 minutes, then transferred to the 70 L batch reactor which was equipped with an overhead condenser, circulation loop, pH probe and various material addition nozzles. The formulation tank was rinsed with dichloromethane (8 L) which was transferred to the batch reactor. The reactor agitator was started and the circulation flow was set at 80 L/min. Phosgene vapor flow to the reactor was initiated (80 g/min flow rate) by the DCS and an initial amount (240 grams, 2.4 moles) was added. The pH of the reaction was maintained at a target of 10.0 by DCS-controlled addition of 33% aqueous NaOH.

After addition of the initial amount of phosgene, the PCP solution was added to the reactor at 500 mL/min flow rate by DCS control while phosgene flow to the reactor continued. Phosgene addition continued until the total set point was reached (2400 grams, 24.3 moles). After completion of the phosgene addition, a sample of the reactor was obtained and verified to be free of un-reacted BPA and free of chloroformate. Mw of a reaction sample was determined by GPC using a UV detector (Mw=36482, PDI=2.8). An additional charge of phosgene was added (200 grams, 2.0 mole) to the reactor. The total amount of excess phosgene was 21%. The reactor was purged with nitrogen then the batch was transferred to the centrifuge feed tank.

To the batch in the centrifuge feed tank was added dilution dichloromethane (8 L) then the mixture was purified using a train of liquid-liquid centrifuges. Centrifuge one separated the brine phase. Centrifuge two removed the triethylamine catalyst by extracting the resin solution with aqueous hydrochloric acid (pH 1). Centrifuges three through eight removed residual ions by extracting the resin solution with DI water. A sample of the resin solution was tested and verified less than 5 ppm each of ionic chloride and residual triethylamine.

The resin solution was transferred to the precipitation feed tank. The resin was isolated as a white powder by steam precipitation followed by drying in a cone shaped vessel using heated nitrogen (210 F). Powder yield 3674 grams. Mw=35779 PDI=3.2.

Sample A6

Sample A6 was made according to the same procedure as Sample A5.

Comparative Example 1

1.5 Mole % DHBP, PTBP Endcap

Sample A9 was made using the following comparative example process to obtain a polycarbonate resin containing 1.5 mole % of 4,4'-dihydroxybenzophenone (DHBP).

A solution of triethylamine (12 mL, 0.16 moles) was prepared in 500 mL of dichloromethane. The triethylamine (TEA) solution was placed in an addition pot connected to the reactor via a dosing pump.

To the formulation tank was added dichloromethane (17 L), DI water (19 L), 4,4'-dihydroxybenzophenone (40 grams, 0.18 moles, 1.5 mole %), bisphenol-A (2778 grams, 12.2 moles), p-tert-butylphenol (PTBP, 48 grams, 0.32 mole, 2.5 mole %) and sodium gluconate (10 grams, iron scavenger). The mixture was stirred for 2 minutes, then transferred to the 70 L batch reactor which was equipped with an overhead condenser, circulation loop, pH probe and various material addition nozzles. The formulation tank was rinsed with

dichloromethane (10 L) which was transferred to the batch reactor. The reactor agitator was started and the circulation flow was set at 80 L/min. To the reactor was added 33% aqueous sodium hydroxide (4340 g, 35.8 moles). The mixture was allowed to stir for 15 minutes while nitrogen sparge was added to the reactor. The nitrogen sparge was stopped, then phosgene vapor flow to the reactor was initiated (13 g/min flow rate) by the DCS control. After addition of 200 g of phosgene and additional amount of 33% aqueous sodium hydroxide (1275 g, 10.5 moles) and DI water (7 L) was added to the reactor. The pH of the reaction was observed to be greater than 12.

Phosgene addition to the reactor was stopped once the total set point was reached (1550 g, 15.7 moles). After completion of the phosgene addition, a sample of the reactor was obtained and tested to confirm the presence of chloroformate by placing approximately 1 mL of sample onto paper tape impregnated with 4-(4-nitrobenzyl)pyridine. Then, the solution of TEA was added to the reactor over the course of 2 minutes and the reaction was allowed to stir and circulate for an additional 15 minutes. A sample of the reactor was then obtained and verified to be free of chloroformate, however a large amount of un-reacted BPA was detected. The sample was analyzed by GPC using a UV detector (Mw=22009, PDI=3.5). An additional charge of phosgene (400 g, 4.0 moles) was added to the reactor. A sample taken from the reactor after the additional phosgene charge; analysis of the sample indicated no unreacted BPA. The Mw of a reaction sample was determined by GPC using a UV detector (Mw=51832, PDI=7.6). The reactor was purged with nitrogen then the batch was transferred to the centrifuge feed tank.

To the batch in the centrifuge feed tank was added dilution dichloromethane (8 L) then the mixture was purified using a train of liquid-liquid centrifuges. Centrifuge one separated the brine phase. Centrifuge two removed the triethylamine catalyst by extracting the resin solution with aqueous hydrochloric acid (pH 1). Centrifuges three through eight removed residual ions by extracting the resin solution with DI water. A sample of the resin solution was tested and verified less than 5 ppm each of ionic chloride and residual triethylamine.

The resin solution was transferred to the precipitation feed tank. The resin was isolated as a white powder by steam precipitation followed by drying in a cone shaped vessel using heated nitrogen (210 F). Powder yield 2087 grams. Mw=47878 PDI=7.9. The observed increase in Mw after charging additional phosgene indicated the polymerization was not complete after addition of the described amount of phosgene. The amount of excess phosgene used in the batch was 57%.

Sample A10

Sample A10 was made according to the same procedure as Sample A9.

Comparative Example 2

1.5 Mole % DHBP, PCP Endcap

Sample A11 was made using the following comparative example process to obtain a polycarbonate resin containing 1.5 mole % of 4,4'-dihydroxybenzophenone (DHBP).

A solution of triethylamine (12 mL, 0.16 moles) was prepared in 500 mL of dichloromethane. The triethylamine (TEA) solution was placed in an addition pot connected to the reactor via a dosing pump.

To the formulation tank was added dichloromethane (17 L), DI water (19 L), 4,4'-dihydroxybenzophenone (40 grams, 0.18 moles, 1.5 mole %), bisphenol-A (2778 grams, 12.2

moles), p-cumylphenol (68 g, 0.32 mole, 2.5 mole %) and sodium gluconate (10 grams, iron scavenger). The mixture was stirred for 2 minutes, then transferred to the 70 L batch reactor which was equipped with an overhead condenser, circulation loop, pH probe and various material addition nozzles. The formulation tank was rinsed with dichloromethane (10 L) which was transferred to the batch reactor. The reactor agitator was started and the circulation flow was set at 80 L/min. To the reactor was added 33% aqueous sodium hydroxide (4340 g, 35.8 moles). The mixture was allowed to stir for 15 minutes while nitrogen sparge was added to the reactor. The nitrogen sparge was stopped, then phosgene vapor flow to the reactor was initiated (13 g/min flow rate) by the DCS control. After addition of 200 g of phosgene and additional amount of 33% aqueous sodium hydroxide (1275 g, 10.5 moles) and DI water (7 L) was added to the reactor. The pH of the reaction was observed to be greater than 12.

Phosgene addition to the reactor was stopped once the total set point was reached (1550 g, 15.7 moles). After completion of the phosgene addition, a sample of the reactor was obtained and tested to confirm the presence of chloroformate by placing approximately 1 mL of sample onto paper tape impregnated with 4-(4-nitrobenzyl)pyridine. Then, the solution of TEA was added to the reactor over the course of 2 minutes and the reaction was allowed to stir and circulate for an additional 15 minutes. A sample of the reactor was then obtained and verified to be free of chloroformate, however a large amount of un-reacted BPA was detected. The sample was analyzed by GPC using a UV detector (Mw=61734, PDI=8.8). An additional charge of phosgene (400 g, 4.0 moles) was added to the reactor. A sample taken from the reactor after the additional phosgene charge; analysis of the sample indicated no unreacted BPA. The Mw of a reaction sample was determined by GPC using a UV detector (Mw=100936, PDI=14.5). The reactor was purged with nitrogen then the batch was transferred to the centrifuge feed tank.

To the batch in the centrifuge feed tank was added dilution dichloromethane (8 L) then the mixture was purified using a train of liquid-liquid centrifuges. Centrifuge one separated the brine phase. Centrifuge two removed the triethylamine catalyst by extracting the resin solution with aqueous hydrochloric acid (pH 1). Centrifuges three through eight removed residual ions by extracting the resin solution with DI water. A sample of the resin solution was tested and verified less than 5 ppm each of ionic chloride and residual triethylamine.

The resin solution was transferred to the precipitation feed tank. The resin was isolated as a white powder by steam precipitation followed by drying in a cone shaped vessel using heated nitrogen (210 F). Powder yield 2263 grams. Mw=88885 PDI=10.9. The observed increase in Mw after charging additional phosgene indicated the polymerization was not complete after addition of the described amount of phosgene. The amount of excess phosgene used in the batch was 57%.

Sample A12

Sample A12 was made according to the same procedure as Sample A11.

Samples A5, A6, A7, and A8 were prepared according to the present disclosure. Samples A9, A10, A11, and A12 are comparative examples that were not prepared according to the present disclosure. Various properties were measured using GPC and a UV detector. The endcap was p-cumylphenol (PCP) or p-tert-butylphenol (PTBP). The Mw and PDI were measured for the powder (Pwd). They are summarized below in Table 1A.

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TABLE 1A

Sample	Process	End Cap	Mole % Endcap	Mole % DHBP	Excess Phosgene	Pwd Mw	Pwd PDI
A5	Soln addn	PCP	2.5	1.5	21	35779	3.2
A6	Soln addn	PCP	2.5	1.5	21	36001	3.0
A7	Soln addn	PTBP	2.5	1.5	21	35935	3.2
A8	Soln addn	PTBP	2.5	1.5	21	35354	3.2
A9	comparative	PTBP	2.5	1.5	57	47879	7.9
A10	comparative	PTBP	2.5	1.5	57	50029	8.1
A11	comparative	PCP	2.5	1.5	57	88885	10.9
A12	comparative	PCP	5.7	1.5	90	33302	4.8

The polydispersity (PDI) of the polymers produced by the processes of the present disclosure was less broad. Pressed films and solutions of the polymers of the present disclosure were also haze free, and the reaction process was more time efficient, in that separate steps were not required for phosgenation and condensation.

Various properties of Samples A1, A2, A3, and A4 were measured using GPC and either a UV detector or an RI detector. The results are also shown in Table 1B. The "lows" columns indicate the weight percentage of chains with a molecular weight below 1000. "Rxn" indicates the measurement of the reaction sample, and "Pwd" indicates measurement of the powder.

TABLE 1B

Sample ID	Process	mol % endcap	Mol % DHBP	Mw UV	PDI UV	Lows % UV	Mw RI	PDI RI	Lows % RI	PDI ratio UV/RI
A1	Soln addn	4.4	1.6	21536	2.3	1.32	21769	2.3	1.2	1.00
A2	Soln addn	4.5	5.1	21454	2.1	1.00	21836	2.3	1.3	0.91
A3	Soln addn	4.5	10.1	21523	2.2	1.01	21476	2.2	1.1	1.00
A4	Soln addn	4.5	20.1	21401	2.1	0.9	21587	2.2	1	0.95

As seen here, all of the solution addition examples had a PDI ratio (UV/RI) of 1.4 or lower. It is noted that the ratios of Sample A2 and Sample A4, which are below 1.0, are likely due to measurement error.

Example 2

Samples of various dimensions were made from a cross-linkable polycarbonate (XPC) copolymer containing bisphenol-A and 1.6 mole % 4,4'-dihydroxybenzophenone (DHBP), and p-cumylphenol (PCP) endcaps, and having an Mw of 21,536. The XPC copolymer was compared to a low-flow bisphenol-A polycarbonate homopolymer having an Mw=31,000 (LF-PC). The flame performance of these plaques was tested before and after UV exposure to 30 J/cm^2 UVA using unfiltered UV light from the Fusion UV system. Chemical resistance was measured by the elongation at break of tensile bars having 3.2 mm thickness. For flame performance, results for 48 hours are reported on the left column, while results for 168 hours are reported on the right column for each example. The results are shown in Table 2.

TABLE 2

Components	D1	D3	D8
DHBP LF XPC (1.6 mol %) (phr)		100	
LF-PC (phr)	100		100
Rimar Salt (phr)	0.1	0.1	

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TABLE 2-continued

Components	D1	D3	D8
Phosphite stabilizer (phr)	0.06	0.06	0.06
XPC (DHBP wt %)	—	1.6	—
Mw		38468	
Mn		9895	
PDI		3.9	
MFR (1.2 kg/300° C., 360 sec)	6.67	6.15	6.51
MFR (1.2 kg/300° C., 1080 sec)	7.17	6.39	7
Gel Thickness (micron)	0	9.75	0
Delta YI	3.4	20.1	3.8

Flame Performance (non-UV exposure)						
Components	D1		D3		D8	
p(FTP) for V0 @ 1.5 mm (48 hr/168 hr)	0	0	0.823	0	0	0
flaming drips	2/3	3/3	0/3	3/3	3/3	3/3
p(FTP) for V0 @ 1.2 mm (48 hr/168 hr)	0	0	0	0	0	0
flaming drips	2/3	3/3	3/3	3/3	3/3	3/3
p(FTP) for V0 @ 1.0 mm (48 hr/168 hr)	0	0	0	0	0	0
flaming drips	3/3	3/3	3/3	3/3	2/3	3/3

TABLE 2-continued

Components	D1		D3		D8	
5 VA @ 1.5 mm (48 hr/168 hr)	Fail	Fail	Fail	Fail	Fail	Fail
Flame Performance (UV exposure)						
p(FTP) for V0 @ 1.5 mm (48 hr/168 hr)	0	0	0.99	0.769	0	0
flaming drips	6/10	7/10	0/18	0/18	5/5	5/5
p(FTP) for V0 @ 1.2 mm (48 hr/168 hr)	0	0	0.982	0.977	0	0
flaming drips	8/10	5/5	0/18	0/18	5/5	5/5
p(FTP) for V0 @ 1.0 mm (48 hr/168 hr)	0.74	0	0.987	0.43	0	0
flaming drips	1/18	5/5	0/18	0/18	6/10	5/5
5 VA @ 1.5 mm	Fail	Fail	Pass	Fail	Fail	Fail
Chemical Resistance (Elongation @ Break)						
As molded bar Acetone @ 0.5% strain	134.2		119.9		124.9	
No UV	10.5		1.5		0.0	
Exposed to UV Acetone @ 1% strain	5.9		97.0		9.2	
No UV	0.0		0.0		0.0	
Exposed to UV	0.0		78.2		0.0	

Example 3

Next, five different XPC resins were tested. The resins were copolymers of bisphenol-A and 4,4'-dihydroxybenzophenone (DHBP), and used PCP endcaps. The first resin

contained 5 mole % DHBP and had a target Mw of about 21,000. The second resin contained 5 mole % DHBP and had a target Mw of about 26,000. The third resin contained 10 mole % DHBP and had a target Mw of about 21,000. The fourth resin contained 10 mole % DHBP and had a target Mw of about 26,000. The fifth resin contained 20 mole % DHBP and had a target Mw of about 21,000. Compositions were made and tested. UV exposure was to 36 J/cm² UVA of filtered UV light in in the Loctite system, with the top facing the UV lamp. Chemical resistance was measured by the elongation at break of tensile bars having 3.2 mm thickness. The results are shown in Table 3. For flame performance, results for 48 hours are reported on the left column, while results for 168 hours are reported on the right column for each example.

XPC-2 polycarbonate formed from bisphenol-A and having 5 mole % 4,4'-dihydroxybenzophenone, remainder bisphenol-A, and p-cumylphenol endcaps and a molecular weight of 26,000 g/mol by polycarbonate standards. The two resins were cast or pressed into films of 40-60 micrometers, supported on glass slides (25×75 mm films).

The films formed from the 12 compositions were then exposed to filtered UV radiation using the Loctite UV system. Only one surface of each film was exposed. The films were irradiated simultaneously for 0.5, 0.75, 1, 2, or 12 J/cm² of UVA energy by exposing the film for 13 seconds, 19.5 seconds, 26 seconds, 54 seconds, or 320 seconds, respectively. The glass transition temperature (Tg) was measured using DSC.

TABLE 3

	F01	F03	F05	F07	F09
5 mole % DHBP @ 21K (phr)	100.00				
5 mole % DHBP @ 26K (phr)		100.00			
10 mole % DHBP @ 21K (phr)			100.00		
10 mole % DHBP @ 26K (phr)				100.00	
20 mole % DHBP @ 21K (phr)					100.00
Rimar Salt (phr)	0.08	0.08	0.08	0.08	0.08
Phosphite stabilizer (phr)	0.06	0.06	0.06	0.06	0.06
MW by UV detector					
No UV exposure	21186	24873	20784	25030	20859
Following UV exposure	25090	29892	24117	29328	24131
Increase	3904	5019	3333	4298	3272
MFR (1.2 kg/300° C., 360 sec)	24.2	11.4	24.2	11.5	25.2
MFR (1.2 kg/300° C., 1080 sec)	25.2	11.9	24.6	12	24.6
Gel Thickness (micron)	22.18	26.50	35.42	36.74	27.06
YI unexposed part	2.68	2.83	3.48	3.80	4.98
YI after 6 passes	9.47	10.24	14.44	12.09	20.68
Delta YI	6.8	7.4	11.0	8.3	15.7
Flame Performance (non-UV exposure)					
Flaming drips out of 3 @ 1.0 mm (48 hr)	3	3	3	3	3
Flaming drips out of 2 @ 1.2 mm (48 hr)	2	0	2	1	2
5 VB @ 1.2 mm (48 hr/168 hr)	Fail Fail	Fail Fail	Fail Fail	Fail Fail	Fail Fail
5 VB @ 1.5 mm (48 hr/168 hr)	Fail Fail	1/2 Fail	Fail Fail	0/2 Fail	Fail Fail
5 VA @ 1.5 mm (48 hr/168 hr)	Fail Fail	Fail Fail	Fail Fail	Fail Fail	Fail Fail
Flame Performance (UV exposure)					
p(FTP) for V0 @ 1.0 mm (48 hr)	0	0.0391	0.6457	0.0651	0.415
flaming drips (out of 20)	2/5	0	1	2	1
p(FTP) for V0 @ 1.2 mm (48 hr)	0.009	0.7247	0.8171	0.3463	0.0716
flaming drips (out of 20)	8	0	0	1	6
p(FTP) for V0 @ 1.5 mm (48 hr)	0.0006	—	—	0.6074	0.3206
flaming drips (out of 20)	5/10	—	—	0	3
5 VB @ 1.2 mm (48 hr/168 hr)	Fail Fail	Fail Pass	Fail Fail	Fail Fail	Fail Fail
5 VB @ 1.5 mm (48 hr/168 hr)	Fail Pass	5/10 drip Pass	7/10 drip Pass	Fail Pass	Fail Pass
5 VA @ 1.5 mm (48 hr/168 hr)	Pass Pass	Pass Pass	Pass Pass	Pass Pass	Pass Pass
Chemical Resistance (Elongation @ Break)					
As molded bar	131.2	136.9	120.6	129.1	96.6
Acetone @ 0.5% strain					
No UV	4.2	2.6	1.0	4.7	Fail
Exposed to UV	101.1	93.4	89.1	87.8	78.5
Acetone @ 1% strain					
No UV	Fail	Fail	Fail	Fail	Fail
Exposed to UV	26.3	92.8	42.4	89.0	50.3

Example 4

Two XPC resins were tested. One was an XPC-1 polycarbonate formed from bisphenol-A and having 20 mole % 4,4'-dihydroxybenzophenone, remainder bisphenol-A, and p-cumylphenol endcaps and a molecular weight of about 21,000 g/mol by polycarbonate standards. The other was an

After exposure, the films were immersed in 10 mL of methylene chloride and monitored for any residual material at 48 hours. The presence of gel was taken as an indicator of crosslinking. The results are provided in Table 4. Crosslinking was indicated with Y if the number of gels was equal to the number of films, i.e. all films formed a continuous gel layer. They were marked with a G if the number of gels was greater

than the number of films, i.e. the gel layer was fragmented into several pieces. If there were no visible gels, the compositions were marked with an N.

Generally, the XPC-1 (20 mole % DHBP) resin created insoluble gel in less than 30 seconds of UV exposure, while the XPC-2 resin created insoluble gel in less than one minute of UV exposure. Generally, the molecular weight increased with UV exposure, indicating that crosslinking occurred.

TABLE 4

Components	PCB-1	PCB-2
XPC-1 (20 mol %)	100	
XPC-2 (5 mol %)		100
Crosslinked @ 0 UVA J/cm^2	N	N
Crosslinked @ 0.5 UVA J/cm^2	G	N
Crosslinked @ 0.75 UVA J/cm^2	G	N
Crosslinked @ 1 UVA J/cm^2	Y	N
Crosslinked @ 2 UVA J/cm^2	Y	G
Crosslinked @ 12 UVA J/cm^2	Y	Y
DSC Tg (° C.) @ 0 UVA J/cm^2	146	146
DSC Tg (° C.) @ 12 UVA J/cm^2	150	147
Mw @ 0 UVA J/cm^2	—	22401
Mw @ 1 UVA J/cm^2	—	25692
Mw @ 2 UVA J/cm^2	—	29374
Mw @ 12 UVA J/cm^2	—	42098
mole % DHBP of composition	20	5

Example 5

Polycarbonates were made from bisphenol-A, 4,4'-dihydroxybenzophenone (DHBP), phosgene, and an end-capping agent. The end-capping agent was either p-cumylphenol (PCP) or p-tert-butylphenol (PTBP).

The polycarbonates were made using two different processes. The first process was by solution addition according to the present disclosure, in which a base was used to regulate the reaction pH. The second process was the conventional process illustrated in German Patent Application DE 2746141 to Bayer, in which the reaction pH was not regulated.

The polycarbonates were produced as powder and then pelletized. The pellets were then extruded to form tensile bars, which were exposed to 36 J/cm^2 UVA of filtered UV light in the Loctite system. The molecular weights were measured after each step. The average gel thickness of the tensile bars was measured as well.

The results are shown in Table 5 below. They are marked as P1 to indicate the first process of the present disclosure was used, or marked as B1 to indicate the conventional process was used. They are also marked with PCP or PTBP to indicate which end-capping agent was used.

TABLE 5

Components	J01	J02	J03	J04
P1 PCP (phr)	100			
P1 PTBP (phr)		100		
B1 PTBP (phr)			100	
B1 PCP (phr)				100
Rimar Salt (phr)	0.1	0.1	0.1	0.1
Phosphite stabilizer (phr)	0.06	0.06	0.06	0.06
wt % DHBP	1.55	1.6	1.5	1.43
Mole % endcap	2.48	1.64	1.96	5.45
MFR (1.2 kg/300° C., 360 sec)	3.43	3.48	4.37	9.6
MFR (1.2 kg/300° C., 1080 sec)	3.47	3.58	4.49	13.6

TABLE 5-continued

Components	J01	J02	J03	J04
Gel Thickness (micron)	2.76	2.57	1.04	0.64
YI unexposed part	4.88	4.31	5.22	6.31
YI after UV exposure	18.67	17.01	15.58	18.22
Delta YI	13.8	12.7	10.4	11.9
Molecular Weight				
Powder				
Mw	36000	35600	49500	50900
Mn	11613	11867	6346	6526
PDI	3.1	3.0	7.8	7.8
Pellet				
Mw	29315	34680	34821	46515
Mn	11453	11874.0	11830	11658
PDI	2.6	2.9	2.9	4
Pellet (RI detector)				
Mw	37259	37415	35818	30040
Mn	12576	13121	11555	7396
PDI	3.0	2.9	3.1	4.1
Tensile bar before exposure to UV				
Mw	31615	31344	30397	25892
Mn	9771	9574	12017	7542
PDI	3.2	3.3	2.5	3.4
Tensile bar after UV exposure				
Mw	46613	46353	44157	37332
Mn	12096	9595	9892	7636
PDI	3.9	4.8	4.5	4.9
Change	14998	15009	13760	11440

In reviewing the data, the polycarbonates produced using the conventional process were much less stable. This was indicated in the changing molecular weights between powder, pellet, and tensile bar before exposure to UV. This was also indicated in the changing PDIs, which suggest that undesired chemistry was occurring during the extrusion into tensile bars. The PDIs of the P1 examples remained between 2.0 and 3.5 through the powder, pellet, and tensile bar production processes. After UV exposure and crosslinking, the molecular weights of the polycarbonates produced using the conventional process were less than the molecular weights of their starting powders.

The present disclosure has been described with reference to exemplary embodiments. Obviously, modifications and alterations will occur to others upon reading and understanding the preceding detailed description. It is intended that the present disclosure be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

The invention claimed is:

1. A process for preparing a photoactive additive from a dihydroxybenzophenone, a diol chain extender, an end-capping agent, a carbonate precursor, a base, a tertiary amine catalyst, water, and a water-immiscible organic solvent, comprising:

combining the dihydroxybenzophenone, diol chain extender, tertiary amine catalyst, water, and water-immiscible solvent to form a reaction mixture;

adding the carbonate precursor to the reaction mixture over a first time period while co-adding the base to regulate the reaction pH;

adding the end-capping agent to the reaction mixture for a second time period while continuing to add the carbonate precursor and the base; and

continuing to add the carbonate precursor and the base to the reaction mixture for a third time period after addition of the end-capping agent is complete to obtain the photoactive additive.

2. The process of claim 1, wherein the carbonate precursor is phosgene, the diol chain extender is bisphenol-A, the base is an alkali metal hydroxide, and the water-immiscible organic solvent is methylene chloride.

3. The process of claim 1, wherein the dihydroxybenzophenone is 4,4'-dihydroxybenzophenone.

4. The process of claim 1, wherein the end-capping agent is dissolved in a solvent prior to being added to the reaction mixture, the solvent being either the water-immiscible organic solvent or water containing a base.

5. The process of claim 4, wherein the end-capping agent is dissolved in a dilute aqueous sodium hydroxide solution.

6. The process of claim 5, wherein the solution contains from about 1 to about 2 moles of NaOH per mole of the end-capping agent, and contains from about 5 wt % to about 20 wt % of the end-capping agent compound.

7. The process of claim 1, wherein a total time period is defined by the sum of the first time period, the second time period, and the third time period; and the second time period in which the end-capping agent is added to the reaction mixture begins at a point from 10% to about 40% of the total time period.

8. The process of claim 1, wherein the reaction pH is regulated to remain between about 8.5 and about 10.

9. The process of claim 1, wherein the end-capping agent is selected from the group consisting of phenol, p-t-butylphenol, p-cumylphenol, octylphenol, and p-cyanophenol.

10. The process of claim 1, wherein the resulting photoactive additive contains less than 2% of low molecular weight molecules.

11. The process of claim 1, wherein the resulting photoactive additive comprises about 0.5 mole % to 50 mole % of the dihydroxybenzophenone.

12. The process of claim 1, wherein the resulting photoactive additive has a weight-average molecular weight of between 17,000 and 80,000 Daltons, as measured by GPC using a UV detector and polycarbonate molecular weight standards.

13. The process of claim 1, wherein the ratio of the PDI measured using a UV detector to the PDI measured using an RI detector is 1.4 or less when using a GPC method and polycarbonate molecular weight standards.

14. The process of claim 1, wherein the resulting photoactive additive has a MFR of 1 to 40 g/10 min measured according to ASTM D1238 at 300° C./1.2 kg/360 sec dwell.

15. The process of claim 1, wherein the resulting photoactive additive maintains a PDI between 2.0 and 3.5 when made into powder, pellet, and tensile bar forms.

16. A process for preparing a photoactive additive from a dihydroxybenzophenone, a diol chain extender, an end-capping agent, a carbonate precursor, a base, a tertiary amine catalyst, water, and a water-immiscible organic solvent, comprising:

combining the dihydroxybenzophenone, diol chain extender, end-capping agent, tertiary amine catalyst, water, and water-immiscible solvent to form a reaction mixture; and

adding the carbonate precursor to the reaction mixture while co-adding the base to regulate the reaction pH to obtain the photoactive additive.

17. The process of claim 16, wherein the carbonate precursor is phosgene, the diol chain extender is bisphenol-A, the

base is an alkali metal hydroxide, and the water-immiscible organic solvent is methylene chloride.

18. The process of claim 16, wherein the dihydroxybenzophenone is 4,4'-dihydroxybenzophenone.

19. The process of claim 16, wherein the end-capping agent is selected from the group consisting of phenol, p-t-butylphenol, p-cumylphenol, octylphenol, and p-cyanophenol.

20. The process of claim 16, wherein the reaction mixture further comprises a phase transfer catalyst.

21. The process of claim 20, wherein the phase transfer catalyst is methyltributylammonium chloride.

22. The process of claim 16, wherein the pH of the reaction mixture is maintained from about 8.5 to about 10 while the carbonate precursor is added to the reaction mixture.

23. The process of claim 16, wherein the carbonate precursor is added to the reaction mixture over a time period of about 15 minutes to about 45 minutes.

24. The process of claim 16, wherein the resulting photoactive additive contains less than 2% of low molecular weight molecules.

25. The process of claim 16, wherein the resulting photoactive additive does not contain residual pyridine.

26. The process of claim 16, wherein the resulting photoactive additive comprises from about 0.5 mole % to 50 mole % of repeating units derived from the dihydroxybenzophenone.

27. The process of claim 16, wherein the resulting photoactive additive has a weight-average molecular weight of between 17,000 and 80,000 Daltons, as measured by GPC using a UV detector and polycarbonate molecular weight standards.

28. The process of claim 16, wherein the resulting photoactive additive has a MFR of about 1 to about 40 g/10 min measured according to ASTM D1238 at 300° C./1.2 kg/360 sec dwell.

29. A process for preparing a photoactive additive from a dihydroxybenzophenone, a diol chain extender, an end-capping agent, a carbonate precursor, a tertiary amine catalyst, water, and a water-immiscible organic solvent, comprising:

combining the dihydroxybenzophenone, diol chain extender, water, and water-immiscible solvent to form a reaction mixture;

adding the carbonate precursor to the reaction mixture to form chloroformate in the reaction mixture while co-adding the base to regulate the reaction pH;

adding the end-capping agent to the reaction mixture and reacting the reaction mixture; and

adding the tertiary amine catalyst to the reaction mixture and reacting the reaction mixture to obtain the photoactive additive.

30. The process of claim 29, wherein the carbonate precursor is phosgene, the diol chain extender is bisphenol-A, the base is an alkali metal hydroxide, and the water-immiscible organic solvent is methylene chloride.

31. The process of claim 29, wherein the dihydroxybenzophenone is 4,4'-dihydroxybenzophenone.

32. The process of claim 29, wherein the end-capping agent is selected from the group consisting of phenol, p-t-butylphenol, p-cumylphenol, octylphenol, and p-cyanophenol.

33. The process of claim 29, wherein the resulting photoactive additive contains less than 2% of low molecular weight molecules.

34. The process of claim 29, wherein the resulting photoactive additive comprises about 0.5 mole % to 50 mole % repeating units derived from the dihydroxybenzophenone.

35. The process of claim 29, wherein the resulting photoactive additive has a weight-average molecular weight of

between 17,000 and 80,000 Daltons, as measured by GPC using a UV detector and polycarbonate molecular weight standards.

36. A process for preparing a photoactive additive from a dihydroxybenzophenone, a diol chain extender, an end-capping agent, a carbonate precursor, a tertiary amine catalyst, water, and a water-immiscible organic solvent, comprising:

pre-reacting the end-capping agent with the carbonate precursor in a tubular reactor to convert the end-capping agent into a monochloroformate;

combining the dihydroxybenzophenone, diol chain extender, tertiary amine catalyst, water, and water-immiscible solvent in a reaction mixture;

adding the carbonate precursor to the reaction mixture over a first time period; and

adding the monochloroformate compound to the reaction mixture throughout the first time period while co-adding the base to regulate the reaction pH to obtain the photoactive additive.

37. The process of claim **36**, wherein the carbonate precursor is phosgene, the diol chain extender is bisphenol-A, the base is an alkali metal hydroxide, and the water-immiscible organic solvent is methylene chloride.

38. The process of claim **36**, wherein the dihydroxybenzophenone is 4,4'-dihydroxybenzophenone.

39. The process of claim **36**, wherein the end-capping agent is selected from the group consisting of phenol, p-t-butylphenol, p-cumylphenol, octylphenol, and p-cyanophenol.

40. The process of claim **36**, wherein the resulting photoactive additive comprises about 0.5 mole % to 50 mole % repeating units derived from the dihydroxybenzophenone.

41. The process of claim **36**, wherein the resulting photoactive additive has a weight-average molecular weight of between 17,000 and 80,000 Daltons, as measured by GPC using a UV detector and polycarbonate molecular weight standards.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO.   : 9,181,390 B2
APPLICATION NO.   : 14/213381
DATED   : November 10, 2015
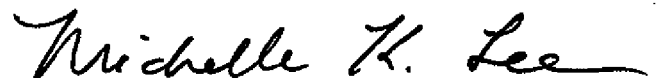INVENTOR(S)   : Hoover et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title Page (60) should appear as follows:

(60) Provisional application No. 61/791,886, filed on Mar. 15, 2013.

(60) Provisional application No. 61/790,222, filed on Mar. 13, 2013.

Signed and Sealed this
Fifteenth Day of March, 2016

Michelle K. Lee

Michelle K. Lee
Director of the United States Patent and Trademark Office

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO.   : 9,181,390 B2   Page 1 of 1
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DATED   : November 10, 2015
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Signed and Sealed this
Eleventh Day of October, 2016

Michelle K. Lee

Michelle K. Lee
Director of the United States Patent and Trademark Office